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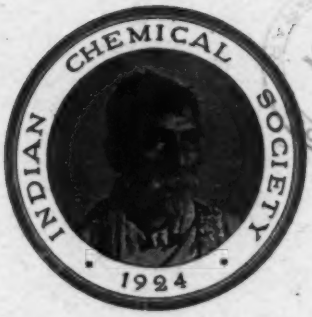

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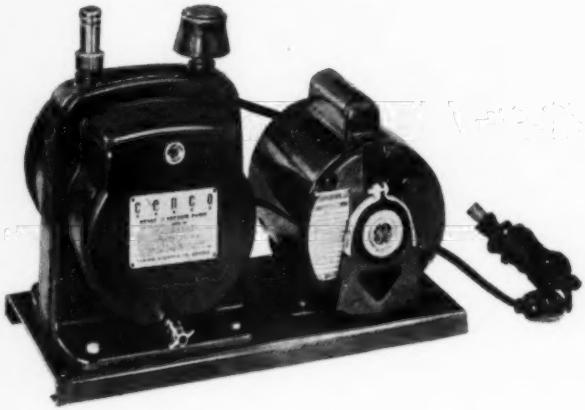

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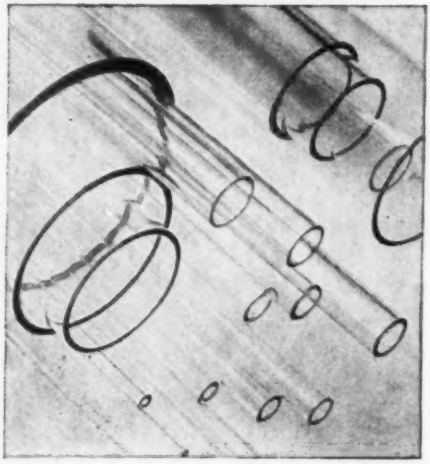

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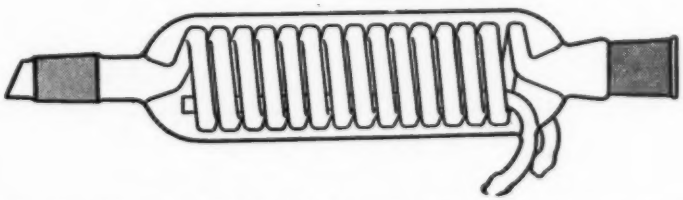

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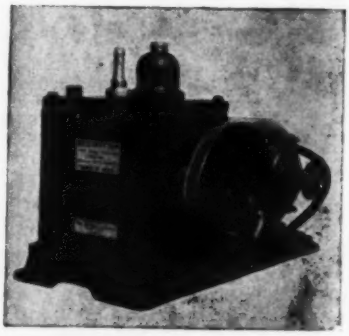

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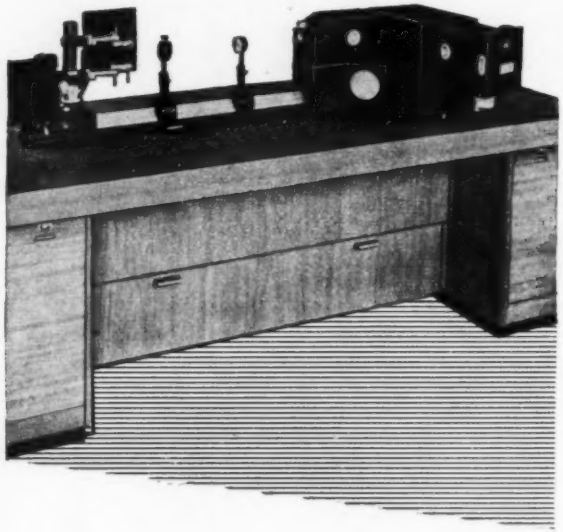

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[Jour. Indian Chem. Soc., Vol. 37, No. 12, 1960]

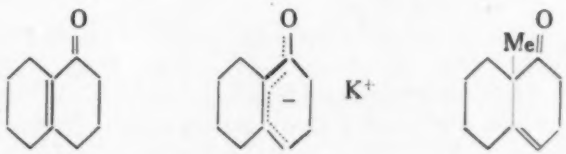
ANGULAR METHYLATION STUDIES ON $\Delta^{4(10)}$-OCTALONE-1

By J. A. K. Quartey

$\Delta^{4(10)}$-Octalone-1 (VI) has been obtained by the Birch reduction of 5:6:7:8-tetrahydro-1-naphthyl hydroxyethyl ether (VII: R=CH_2CH_2OH), followed by mild acid hydrolysis. The octalone (VI) cannot be methylated in the angular position under the usual conditions. On catalytic hydrogenation in a neutral medium it affords almost quantitatively *trans*-1-decalone (IX).

Abundant evidence has been obtained that the angular methyl groups can be omitted in steroid analogues with retention of considerable hormonal activity. Thus, as has been established, 19-nortestosterone (Birch, *J. Chem. Soc.*, 1950, 367) and 19-norprogesterone (Djerassi *et al.*, *J. Amer. Chem. Soc.*, 1953, **75,** 4440) possess a high order of activity (see also Djerassi *et al.*, *ibid.*, 1953, **75,** 4117; 1954, **76,** 4092; 1955, **77,** 148). Johnson *et al.* (*ibid.*, 1953, **75,** 4866) found 18-nor-D-homoandrostan-3 : 17a-dione to be as active as the natural androstan-3 : 17-dione. Earlier, Birch and Quartey (*Chem. & Ind.*, 1953, 489) had produced evidence that an 18 : 19-*bis*-nor-D-homosteroid possessed some activity, and had advanced the view that *bis*-nor-D-homo analogues of steroid hormones might in general be expected to show considerable activity, provided that the *trans* configuration was present at the C/D ring-junction. Johnson *et al.* (*J. Org. Chem.*, 1954, **19,** 670), however, found that 18 : 19-*bis*-nor-D-homotestosterone had little activity. Thus the question of the structural requirements for hormonal activity needs further investigation.

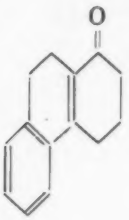
In the general case it is desirable, however, to have the angular methyl groups present, and methods have been examined for their introduction into the preformed nucleus (Birch, Quartey, and Smith, *J. Chem. Soc.*, 1952, 1768). These methods depend on the supposition that if compounds of type (I) can be converted into the salts of the mesomeric anion (II), addition of a methyl cation may be expected to yield predominantly the desired product (III).



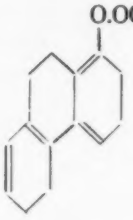
(I) (II) (III)

The double bond in (I) is extremely stable, the equilibrium between simple α : β- and β : γ-unsaturated ketones in the presence of acid or basic catalysts being generally largely in favour of the α : β-isomer. Hence indirect methods are required for the formation of the salt of the mesomeric anion (II); though in some cases the requisite salts may be directly produced by the

action of the correct enolising agent. An attempt to obtain such a salt from (IV) by conversion first to the enol-acetate failed, though the enol-benzoate (V) could be obtained (in poor yield). The acid hydrolysis of this enol-benzoate is as facile as that of enol-ethers.



(IV)



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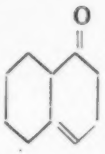

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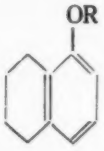


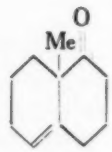
(VII)

The usual Birch (metal-alcohol/liquid ammonia) reduction of aromatic compounds of type (VII), followed by vigorous acid hydrolysis of the dihydrobenzene "acids", results in the conjugated ketone of type (I). Birch (*J. Chem. Soc.*, 1944, 430) reported that the reduction and subsequent hydrolysis of (VII : R=Me) gave only a trace of (I). This has been confirmed, the yield of (I) being 3% calculated on the isolated 2 : 4-dinitrophenylhydrazone. It has been found, however, that the ether (VII : R=$CH_2.CH_2OH$), is reduced smoothly and affords a good yield of the ketone on hydrolysis (64%). Milder conditions of hydrolysis have been found to yield 34% of β : γ-unsaturated ketone (VI). This unconjugated isomer has been examined for angular methylation.

An angular methyl group could not be introduced into (VI) to furnish (III) under the usual conditions with potassium amide in liquid ammonia, or even in boiling toluene, followed by methyl iodide. The ketone (VI) was recovered unchanged from these experiments. It has not been possible to obtain satisfactory analyses for the ketones (I) and (VI) even after purification through the semicarbazones.

(VIII)

(IX)



(X)

Any possibility of the formation of a spiroketal, such as (VIII), which corresponds more closely to the analysis, can, however, not be sustained since the ketones were obtained by acid hydrolysis (cf. Birch, Murray, and Smith, *J. Chem. Soc.*, 1951, 1945). Furthermore, the ketone (VI) was isolated as the sodium bisulphite addition compound, and the other (I) not furnishing such an adduct; the derivatives of (I) and (VI) gave the correct analyses.

The ketone (VI) on treatment with acid is converted into (I), which can itself be directly obtained by more vigorous hydrolysis of the reduction product of (VII : R=CH_2CH_2OH). The ultraviolet characteristics of (I), λ_{max} 244 mμ, ϵ_{max} 8,800 ; λ_{min} 286 mμ, ϵ_{min} 67.6 ; λ_{max} 301-304 mμ, ϵ_{max} 74.7, are in agreement with those reported for $\Delta^{9(10)}$-octalone-1 by Campbell and Harris (*J. Amer. Chem. Soc.*, 1941, **63**, 2721) who record λ_{max} 243 mμ, ϵ_{max} 10,000 ; λ_{max} 305 mμ, ϵ_{max} 63.1.

The ketone (VI) is hydrogenated almost quantitatively, with palladium-charcoal in ether, to a ketone, which has been characterised as *trans*-1-decalone (IX), the production of the more stable *trans* configuration being in accordance with the expectation (cf. the hydrogenation of unsaturated steroids). It is thus clear that the starting material was substantially the pure ketone (VI), and the conclusion then is that it cannot be methylated in the angular position by the usual procedure, *i.e.*, the energy required to form the resonant ion (II) is not reached though a positive result would have been helpful in deciding between the isomeric ketones (III) and (X), obtained by various earlier workers, e.g. Plentl and Bogert (*J. Org. Chem.*, 1941, **6**, 669).

EXPERIMENTAL

1 : 2 : 3 : 4 : 9 : 10-*Hexahydro*-1-*ketophenanthrene* (IV).—Resorcinol dimethyl ether (20 g.) was dissolved in ethanol (150 c.c.) and added to liquid ammonia (1.5 litres). Sodium (9 g.) in thin slices was added; after the reaction water (1 litre) was slowly added. The mixture was extracted with ether (4×100 c.c.), the ether extract washed once with water (150 c.c.), and dried (K_2CO_3). It was then evaporated under nitrogen under reduced pressure and the product distilled to afford 1 : 4-dihydro-2 : 6-dimethoxybenzene, b.p. 86°/12 mm, yield 16.8 g. (83%).

To a solution of potassium amide (from the metal, 2.25 g., 1.1 mole) in liquid ammonia (*ca.* 200 c.c.) was added the above dihydro ether (14.0 g.), the solution changing to a deep red colour with the formation of the potassium salt. The solution was left for 10 minutes and then phenethyl bromide was slowly added with swirling until the red colour was discharged (9.3 g. of the bromide). Water (100 c.c.) was cautiously added, and the product extracted with ether. The ether extract was washed once with water, and evaporated. 1 : 3-Dimethoxy-2-phenethyl*cyclo*hexa-3 : 6-diene, so obtained, was hydrolysed with 2*N*-HCl (10 c.c.) for 10 minutes on the steam bath. The solution was cooled, extracted with ether, and the ether extract shaken with small portions of sodium hydroxide solution (10%) until acidification gave no further precipitate. The crystalline solid so obtained was removed by filtration and crystallised from ethyl acetate-petrol ether (60-80°) (1 : 1) to furnish colorless prisms of 2-phenethyl-*cyclo*hexane-1 : 3-dione, m.p. 147°, in 85% yield, based on the dihydro ether. The above diketone (3.0 g.) was added as a fine powder to a stirred solution of phosphoric anhydride (12 g.) in phosphoric acid (1.75 c.c.). The solution was kept under nitrogen at 150° for 45 minutes, after which it was cooled. Water was added, the product extracted with ether, the ether extract dried (Na_2SO_4), and evaporated. Purification was achieved by chromatography on activated alumina (30 g.) when the 1 : 2 : 3 : 4 : 9 : 10-*hexahydro*-1-*ketophenanthrene* was eluted with ether-petrol ether (40-60°) (2 : 1) and crystallised from petrol ether (b.p. 40-60°) to provide colorless prisms, m.p. 48-49°, yield 1.5 g., 55% based on the dione. (Found : C, 84.8 ; H, 7.15. Calc. for $C_{14}H_{14}O$: C, 84.8 ; H, 7.1%). Johnson, Johnson, and Petersen (*J. Amer. Chem. Soc.*, 1946, **68**, 1928) record m.p. 49-49.5° for the material purified through the semicarbazone.

The *oxime* was crystallised from ethanol, m.p. 140°. (Found : N, 6.4. Calc. for $C_{14}H_{15}ON$: N, 6.6%). Johnson, Johnson, and Petersen (*loc. cit.*) record m.p. 141-42°.

The above ketone, when heated with acetic anhydride together with a trace of *p*-toluenesulphonyl chloride on the steam bath for 1.5 hours under nitrogen, was recovered unchanged, m.p. 48-49°, undepressed by the starting material.

2 : 3 : 9 : 10-*Tetrahydrophenanthrene*-1-*benzoate* (V).—The above ketone (1.0 g.) was heated with benzoyl chloride (5 c.c.) at 120-30° under nitrogen for 3 hours. The solution was cooled, poured into dilute 5% NaOH solution, and left overnight. It was extracted with ether, the ether

extract washed, dried (K_2CO_3), and evaporated. The product was taken up in little of ether and put on a column of activated alumina (*ca.* 30 g.). The chromatogram was developed and after a preliminary first fraction of petrol ether (40-60°), the product was eluted with ether—petrol ether (40-60°) (1 : 1).

2 : 3 : 9 : 10-*Tetrahydrophenanthrene*-1-*benzoate*, obtained in poor yield, was crystallised from ether, m.p. 134°. (Found : C, 83.1 ; H, 5.8. $C_{21}H_{18}O_2$ requires C, 83.4 ; H, 6.0%). The infrared absorption spectrum in nujol mull showed bands at the following wave lengths (μ) : (3.95N), 5.77s, 6.05m, 6.25m, 6.31m, 6.40m, (6.90N), (727N), 7.64w, 7.90s, 7.97s, 8.35m, 8.57s, 8.90s, 9.20s, 9.37m, 9.75m, 10.00w, 11.15w, 11.36w, 11.60w, 12.45w, 12.70w, 13.24s, 13.70m, 14.06s, 14.63w. (s = strong, m = medium, w= weak).

With Brady's reagent it gave 1 : 2 : 3 : 4 : 9 : 10-hexahydro-1-ketophenanthrene-2 : 4-dinitrophenylhydrazone.

5 : 6 : 7 : 8-*Tetrahydro*-1-*naphthylhydroxyethyl Ether* (VII : R=CH_2CH_2OH).—Commercial α-naphthol (50 g.) was reduced with sodium (40 g.) in boiling amyl alcohol (600 g.) over a period of 2 hours. The solution was cooled, poured into water, and the amyl alcohol steam-distilled. After cooling, the sodium salt was acidified with HCl (dil.), the solution extracted with ether, the ether extract washed, dried (Na_2SO_4), evaporated, and distilled under nitrogen. Unless the distillation was under nitrogen, appreciable decomposition of the product occurred, this being presumably due to aromatisation. 5 : 6 : 7 : 8-Tetrahydro-1-naphthol boiled at 144°/14 mm (41 g.) and it was crystallised from petrol ether (40-60°), m.p. 74-75°. (Found : C, 81.1 ; H, 7.85. Calc. for $C_{10}H_{12}O$: C, 81.1 ; H, 8.1%). Bamberger and Bordt (*Ber.*, 1890, **23,** 215) record m.p. 68.5-69°. The methyl ether (VII : R=Me) (29 g. from 34 g. of the phenol) boiled at 124°/ 10mm, n_D^{20} 1.566.

To the above 5 : 6 : 7 : 8-tetrahydro-1-naphthol (30 g.), dissolved in 10% NaOH solution (160 c.c.) and heated on the steam bath, was slowly added with stirring ethylene chlorhydrin (80 g., 5 moles) in small portions, 10% NaOH solution being added to keep the mixture alkaline. At the end of the addition of the ethylene chlorhydrin, a further 150 c.c. of 10% NaOH solution was added, the mixture stirred for a further ½ hour, cooled and extracted with ether. The ether extract was washed, dried (Na_2SO_4), evaporated, and distilled under nitrogen. The product distilled almost quantitatively (35 g., 90% of the theoretical) as a viscous yellow oil, b.p. 135-37°/ 0.1 mm.

5 : 6 : 7 : 8-*Tetrahydro*-1-*naphthylhydroxyethyl ether* (VII : R = CH_2CH_2OH) was crystallised from petrol ether (40-60°) in dimorphic white needles, m.p. 41-42°, which on repeated recrystallisation gave white plates, m.p. 51°. (Found : C, 75.2 ; H, 8.2. $C_{12}H_{16}O_2$ requires C, 75.0 ; H, 8.3%).

$\Delta^{4(10)}$ -*Octalone*-1 (VI).—5 : 6 : 7 : 8-Tetrahydro-1-naphthylhydroxyethyl ether (30 g.), dissolved in ethanol (600 c.c.), was added to liquid ammonia (*ca.* 1.5 litres). Sodium (86 g., 6 moles) in thin slices was added with shaking. After the reaction, water (1 litre) was gradually added and the solution extracted with ether. The ether extract was washed, dried (K_2CO_3), evaporated, and the product distilled almost quantitatively under nitrogen. After two preliminary fractions, b.p. 34°/0.05 mm and 70°/0.05 mm, 3 : 5 : 6 : 7 : 8 : 9-hexahydro-1-naphthylhydroxyethyl ether (20 g.) was collected at 123-25°/0.05 mm (66% yield). The above hexahydro-1-naphthylhydroxyethyl ether was dissolved in ether (*ca.* 50 c.c.), 0.5 *N*-HCl (*ca.* 25 c.c.) added, and the whole shaken for 3.5 hours at room temperature (*ca.* 20°). The ether layer was separated,

the aqueous solution extracted with ether, and the combined ether extract reduced to *ca.* 15 c.c. This was left shaking with freshly prepared saturated sodium bisulphite solution (*ca.* 25 c.c.) overnight. The sodium bisulphite adduct (19 g.) was filtered and thoroughly washed with ether.

The combined ether filtrate and washings were concentrated and shaken again for *ca.* 4 hours with saturated sodium bisulphite solution, when a further 6 g. of the bisulphite adduct was recovered. The sodium bisulphite adduct (25 g.) so obtained was decomposed with *N* sodium carbonate (300 c.c.) and ether (150 c.c.), and the aqueous solution again extracted with ether. The combined ether extract was washed once with water, dried (K_2CO_3), evaporated, and distilled under nitrogen. The $\Delta^{4(10)}$-octalone-1 (8 g.) distilled almost quantitatively as a colorless liquid at 112°/14 mm, $n_D^{22.5}$ 1.507. (Found : C, 77.8; H, 9.4. $C_{10}H_{14}O$ requires C, 80.0 ; H, 9.3%). λ_{min} 270 mμ ϵ_{min} 25 ; λ_{max} 289-290 mμ, ϵ_{max} 30.

With Brady's reagent in the cold the orange 2 : 4-dinitrophenylhydrazone was obtained. If this was quickly filtered and washed with ethanol, it could be crystallised from the latter, m.p. 157°. Treatment with Brady's reagent in the hot furnished the deep red derivative of $\Delta^{9(10)}$-octalone-1. Its semicarbazone was crystallised from ethanol ; m.p. varied from 218° (decomp.) to 228° (decomp.) with the rate of heating. (Found : C, 63.3 ; H, 8.4 ; N, 20.8. $C_{11}H_{17}ON_3$ requires C, 63.2 ; H, 8.2 ; N, 20.3%).

$\Delta^{9(10)}$ *-Octalone*-1 (I).— 5 : 6 : 7 : 8-Tetrahydro-1-naphthylhydroxyethyl ether (20 g.) in ethanol (500 c.c.) was reduced with sodium (50 g.) in liquid ammonia (*ca.* 1.5 litre) as above. The product was worked up as above and the resulting oil hydrolysed with 2*N*-HCl (25 c.c.) on the steam bath for ½ hour, extracted with ether and the ether extract washed, dried (Na_2SO_4), and distilled under nitrogen. After a preliminary fraction (1.5 g.), b.p., 110-20°/14 mm, the bulk of the product (7.7 g.) distilled at 120-40°/14 mm and boiled at 131-33°/14 mm on redistillation. (Found : C, 77.7 ; H, 9.5. Calc. for $C_{10}H_{14}O$: C, 80.0 ; H, 9.3%). From the distillation residue 4.5 g. of the starting material was recovered by crystallisation from petrol ether (b.p. 40-60°). Yield of $\Delta^{9(10)}$ -octalone-1, based on reacting material, was therefore 64%. For the material purified via the semicarbazone, the analysis was still incorrect. (Found : C, 76.2 ; H, 9.2%), $n_D^{21.5}$ 1.517, but the ultraviolet absorption spectrum was in accordance with expectation : λ_{max} 244 mμ, ϵ_{max} 8,800 ; λ_{min} 286 mμ, ϵ_{min} 67.6 ; λ_{max} 301-304 mμ, ϵ_{max} 74.7 (cf. Campbell and Harris, *loc. cit.*). The $\Delta^{9(10)}$ -octalone-1 semicarbazone was crystallised from ethanol, m.p. 242-44° (decomp.). (Found: C, 62.7; H, 8.2; N, 20.2. Calc. for $C_{11}H_{17}ON_3$: C, 63.2; H, 8.2; N, 20.3%). Cook and Lawrence (*J. Chem. Soc.*, 1937, 817) report semicarbazone m.p. 242-43°; Hückel and Naab (*Annalan*, 1933, **502,** 136) report m.p. 244° (decomp.).

The 2 : 4-dinitrophenylhydrazone was found to be polymorphic. Crystallised from ethyl acetate it had m.p. 224-25°. (Found : C, 58.0 ; H, 5.7 ; N, 17.15. Calc. for $C_{16}H_{18}O_4N_4$: C, 58.2 ; H, 5.5 ; N, 17.0%) and from benzene it had m.p. 266-67° (Found : C, 58.0 ; H, 5.7 ; N, 17.25. Calc. for $C_{16}H_{18}O_4N_4$: C, 58.2 ; H, 5.5 ; N, 17.0%). Cook and Lawrence (*loc. cit.*) report m.p. (xylene) 266-67° (decomp.) ; Birch (*J. Chem. Soc.*, 1944 430) gives m.p. 264°. The $\Delta^{9(10)}$ -octalone-1 oxime was crystallised from aqueous methanol, m.p. 144-45°. Cook and Lawrence (*loc. cit.*) report m.p. 144-45° ; Hückel and Naab (*loc. cit.*) report m.p. 148°.

trans-α-*Decalone* (IX).— $\Delta^{4(10)}$ -Octalone-1 (5 g.) was dissolved in ether and hydrogenated with 5% Pd-C catalyst. The absorption of hydrogen was rather slow at first, but more rapid later, one molar proportion of hydrogen being absorbed in the course of a day.

The product was filtered from the catalyst, dried (Na_2SO_4), and distilled under nitrogen to yield 5 g. of *trans*-α-decalone, b.p. 107°/15 mm, n_D^{14} 1.490. (Found: C, 78.8; H, 10.8. Calc. for $C_{10}H_{16}O$: C, 78.9; H, 10.5%). The product crystallised on standing overnight in the refrigerator.

The 2: 4-dinitrophenylhydrazone was crystallised from benzene, m.p. 231° (decomp.). (Found: C, 57.7; H, 5.6; N, 17.1. Calc. for $C_{16}H_{20}O_4N_4$: C, 57.8; H, 6.0; N, 16.7%).

The semicarbazone was crystallised from methanol, m.p. 227-28°. (Found: C, 63.1; H, 8.9; N, 19.9. Calc. for $C_{11}H_{19}ON_3$: C, 63.2; H, 9.1; N, 20.1%).

The oxime was crystallised from ethanol as needles, m.p. 167-68°, which sublimed at 58°/0.1 mm. (Found: C, 72.4; H, 10.4; N, 8.0. Calc. for $C_{10}H_{17}ON$: C, 71.9; H, 10.2; N, 8.4%).

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A STUDY OF VISCOSITY OF AQUEOUS SOLUTIONS OF POTASSIUM DICHROMATE•

BY S. ALAMELU AND C. V. SURYANARAYANA

Viscosity of aqueous solutions of potassium dichromate over a wide range of concentrations up to saturation has been determined at temperatures ranging from 30° to 60°. The variation of viscosity with temperature at any given concentration has been found to obey Andrade's exponential equation. The variation of viscosity with concentration at any given temperature has been found to obey another exponential equation, first observed by Suryanarayana and Venkatesan.

The purpose of the present investigation is two-fold, firstly to verify the equation of Suryanarayana and Venkatesan (*Acta Chim.*, Hung., 1958, **16,** 149, 339, 345; *Trans. Faraday Soc.*, 1958, **54,** 1709; *Bull. Chem. Soc., Japan*, 1958, **31,** 442; *Monatsh.*, 1958, **89,** 824) and secondly to examine the applicability of the equation of Andrade (*Nature*, 1930, **125,** 309) as observed to be applicable to solutions of electrolytes by several others (Berl *et al.*, *Z. physikal. Chem.*, 1931, **152,** 284; Joshi and Solanki, this *Journal*, 1940, **17,** 630; Ram Gopal, *ibid.*, 1953, **30,** 708; Suryanarayana and Venkatesan, *Acta Chim.*, Hung., 1958, **16,** 451).

EXPERIMENTAL

Viscosity and density were determined as described in our earlier publications (*loc. cit.*).

Solubility data were obtained from Seidell ("Solubilities of Organic and Inorganic Compounds", Vol. I, Van Nostrand Co., New York, 1940) and A. Comey and D. Hahn ("A Dictionary of Chemical Solubilities, Inorganic", The Macmillan Co., London, 1921). Results obtained are recorded in Table I.

TABLE I

Molality.	Mole frac.	Viscosity (in centipoises) at 30°.	35°.	40°.	45°.	50°.	55°.	60°.	Const. of eq. (2). *A.*	*B.*	E_{vis} (calc.)
0.280	0.005019	0.8335	0.7519	0.6841	0.6238	0.5762	0.5318	0.4903	0.002338	1778	3534
0.335	0.005998	0.8383	0.7563	0.6874	0.6269	0.5813	0.5348	0.4935	0.002375	1775	3529
0.390	0.006977	0.8424	0.7600	0.6907	0.6305	0.5857	0.5378	0.4968	0.002438	1769	3517
0.445	0.007952	0.8487	0.7679	0.6993	0.6378	0.5919	0.5441	0.5020	0.002531	1761	3499
0.500	0.008928	0.8553	0.7745	0.7060	0.6439	0.5987	0.5495	0.5071	0.002621	1753	3483
0.555	0.009900	0.8592	0.7789	0.7098	0.6492	0.6023	0.5542	0.5118	0.002765	1738	3453
0.6124	0.019100	0.8648	0.7823	0.7125	0.6533	0.6059	0.5571	0.5169	0.002900	1725	3428
Saturation		0.8664	0.7975	0.7485	0.6984	0.6615	0.6198	0.5841	0.001115	1317	2619
Molality at saturation ..		0.6798	0.7938	0.9179	1.0870	1.2580	1.4280	1.5980			
Mole fraction at saturation		0.0121	0.0141	0.0163	0.0192	0.0222	0.025	0.02798			
η_0 (extrapol.) ..		0.8072	0.7261	0.6561	0.5984	0.5495	0.5093	0.4690			
η_0 (from Lange) ..		0.8007	0.7225	0.6560	0.5988	0.5494	0.5064	0.4688			
B (calc.) ..		0.0760	0.0951	0.1129	0.1506	0.1892	0.1986	0.2515			
B (obs.) ..		0.0787	0.0988	0.1320	0.1538	0.1857	0.2022	0.2207			

DISCUSSION

A plot (not shown) of log η_i vs. C_p (the ratio of the mole fraction of the solute at the molal concentration under consideration to that at saturation) provides a straight line at each temperature. It is clear that aqueous solutions of potassium dichromate obey the equation of Suryanarayana and Venkatesan (*loc. cit.*) :

$$\eta_i = \eta_{io} \exp. [B' C_p] \quad .. \quad (1)$$

The η_{io} values computed from the intercepts on the graph compare favourably with the values of viscosity of water at the respective temperatures. Similarly, the values of the constant B', computed from the slope at different temperatures excepting at 40° and 60°, compare well with the ln $(\eta_{i\ sat}/\eta_{io})$ at saturation obtained experimentally.

Plots of log η_i vs. $1/T$ (not shown) are linear for all the eight concentrations, thus proving the applicability of Andrade's equation,

$$\eta_i = A. \exp. [-B'/T] \quad .. \quad (2)$$

The last three columns of the table show the values of the constants A and B of equation (2). Eyring *et al.* (*J. Phys. Chem.*, 1937, **41**, 249 ; *J. Chem. Phys.*, 1937, **5**, 726) derived Andrade's equation in the form :

$$\eta_i = A. \exp. [-E_{vis}/RT] \quad .. \quad (3)$$

where E_{vis} is the energy of activation for viscous flow. The last column of the table shows almost the same value for E_{vis} at all concentrations excepting for the saturated concentrations for which it is smaller.

Equations (2) and (3) were originally meant to apply to pure liquids. We have shown from works in this laboratory that several electrolyte solutions obey equations (2) and (3). This points to a fundamentally same basis of viscosity both in pure liquids and solutions. We have indicated in different contexts that internal pressure of a liquid medium may perhaps be such a basis on which a generalised theory of viscosity of liquids may be built.

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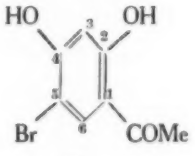
SYNTHESIS OF 2′: 4′-DIHYDROXY-5′-BROMOCHALKONE DERIVATIVES. EFFECT OF BROMINE ATOM AND A FREE HYDROXY GROUP IN THE PHENYL RING ON THE FORMATION OF FLAVONOLS

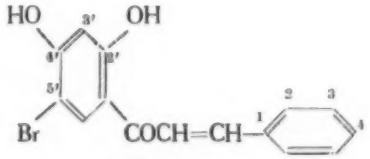
By B. J. Ghiya and M. G. Marathey

2′ : 4′-Dihydroxy-5′-bromochalkones have been synthesised by condensing 2:4-dihydroxy-5-bromoacetophenone with aromatic aldehydes in presence of 40% NaOH and have been converted into their respective flavonols.

Substituted acetophenones have been condensed with aldehydes to obtain the corresponding chalkones (Göschka and Tambor, *Ber.*, 1911, **44,** 3503; Shinoda *et al.*, *J. Pharm. Soc., Japan,* 1929, **49,** 123; Saiyad *et al.*, *J. Chem. Soc.*, 1937, 1737). Resacetophenone condenses rather with difficulty with the aldehydes like benzaldehyde, anisaldehyde, etc. Monomethyl ether of resacetophenone and its monobromo derivatives afford chalkones and flavonols easily (Marathey and Athavale, this *Journal*, 1954, **31,** 654). So it will be of interest to ascertain whether monobromo-resacetophenone condenses with aldehydes like benzaldehyde, anisaldehyde, nitrobenzaldehyde, and piperonal. Bromination of the resacetophenone in acetic acid medium yielded a product which was found identical with 2: 4-dihydroxy-5-bromoacetophenone (Delhiwala and Shah, *Proc. Ind. Acd. Sci.*, 1941, **13A,** 352). The condensation of the ketone with different aldehydes shows that the presence of the bromine atom in the nucleus together with two hydroxy groups facilitates the formation of chalkone; but its presence hinders to some extent the formation of flavonol.



(I)



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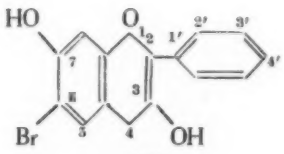

(III)

EXPERIMENTAL

2: 4-*Dihydroxy-5-bromoacetophenone.*—To a solution of resacetophenone (0.7 g.) in 60% acetic acid (5 c.c.) was added a 25% solution of bromine (3.2 c.c.) in acetic acid. The solution became hot (exothermic reaction) and yellowish white crystals began to appear on scratching the sides of the beaker. The crude product after filtration at the pump was crystallised from glacial acetic acid as white crystals (0.5 g.), m.p. 164°. (Found: Br, 34.0. Calc. Br, 34.6%). It dissolves in NaOH solution and develops a deep brown coloration with ethanolic ferric chloride. It is soluble in common organic solvents but is insoluble in water (cf. resacetophenone).

The condensation of ketone with (*i*) benzaldehyde, (*ii*) *m*-nitrobenzaldehyde, (*iii*) anisaldehyde, and (*iv*) piperonal was carried out in the following manner:

To a solution of the ketone (0.5 g.) in ethanol (10 c.c.) was added the aldehyde (1 c.c. or 1 g.). To the homogeneous solution 40% NaOH solution (2 c.c.) was added and the mixture was left for about 36 hours. The solution was acidified, treated with $NaHCO_3$ solution to remove the acid formed in the side reaction, and the crude mass was crystallised from glacial acetic acid in each case. The yield, m.p., and the m.p. of the acetal derivatives are recorded in Table I.

TABLE I

Chalkone.

Aldehyde.	Yield.	M.P.	M.P. of acetal derivative.	% Bromine. Found.	Calc.
Benzaldehyde	0.32 g.	162°	..	24.6	25.0
m-Nitrobenzaldehyde	0.30	213°	235°	21.3	21.9
Anisaldehyde	0.35	173°	166°	22.5	22.9
Piperonal	0.37	280°	130°	21.5	22.0

It is interesting to note that the ketone also condenses smoothly with the aromatic aldehyde (excluding hydroxyaldehydes) by the sodium peroxide method (Marathey, *J. Univ. Poona*, 1956, **8**, 76). This method has the advantage over the other methods in having the time required reduced from 36 hours to 30 minutes and the yield to the same extent.

The above chalkones were condensed into their respective flavonols by the sodium peroxide method (Marathey, *loc. cit.*). The m.p.s. of the flavonols are recorded in Table II.

TABLE II

Flavonol.	M.P.
7-Hydroxy-6-bromo-	168°
7-Hydroxy-6-bromo-3′-nitro-	240°
7-Hydroxy-6-bromo-4′-methoxy-	235°
7-Hydroxy-6-bromo-3′:4′-dioxymethelene-	240°

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POLAROGRAPHIC STUDY OF METAL ION COMPLEXES WITH GLOBIN. PART II*. COBALT, NICKEL, ZINC, AND CADMIUM AT *p*H 5.0 AND 6.6

BY G. H. AHUJA AND C. S. NARWANI

Polarograms of Co, Ni, Zn, and Cd at various concentrations (0.0075-0.02 *M*) in presence of globin at *p*H 5.0 and at 37° show that the diffusion currents in presence of 1.0% globin are less than that in 0.01%, leading to the conclusion that the metal ions form complexes with globin, the -COOH groups of which ionise between *p*H 2.0 and 5.5. In presence of 1.0% globin the diffusion current decreases with time and is constant after 75 minutes in case of Co, Ni, and Zn and 60 minutes in case of Cd. The number of g. atoms of each metal combined with one g. molecule of globin has been calculated. The maximum number of metal atoms combined with one molecule of globin is found to be 24 in the case of Zn; 20 atoms of the bivalent metal are accounted for 40 -COOH and 4 for 8 -SH groups present in one molecule of globin. Lower values at different concentrations of other metals may be attributed to the ionisation of protein-bound metal.

At *p*H 6.6, under the same conditions as mentioned above, the number of g.atoms of Co, Ni, Zn, and Cd combined with one g.molecule of globin has been found to be 18 to 20. Since the imidazole group ionises between *p*H 6.0 and 8.0, it is presumed that there are maximum 40 histidine residues in one molecule of globin.

Polarograms of Co^{2+} and Ni^{2+} ions in presence of 1.0% globin solution at *p*H 6.6 and at 37° were studied by the authors previously (*J. Univ. Bombay*, 1958, **26**, Part II, 15) and the metal ions were found to react with globin, combination taking place at the imidazole groups of histidine residues, which ionised between *p*H 6.0 and 8.0. The object of the present work was to study the polarograms of Co^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+} ions in presence of 1.0% globin at *p*H 5.0 and 6.6 and at 37°. Since imidazole group of histidine residue of the protein does not ionise at $pH < 6.0$, as shown by Tanford (*J. Amer. Chem. Soc.*, 1952, **74**, 211), the metal ions are expected to replace the H of -COOH groups, which ionise between *p*H 2.0 and 5.5 according to the same author.

EXPERIMENTAL

The apparatus, general technique and the chemicals used were as described by the authors in Part I (*loc. cit.*). The molecular weight of globin was determined by deducting the amount of heme from the M.W. of hemoglobin (63,136), determined by the authors from the quantity of iron in a weighed portion of homoglobin ; it was found to be 60,672.

Solutions of Co, Ni, Zn, and Cd acetates (E. Merck's C.P.) were prepared and standardised by chemical analysis. *p*H of the solutions used for polarographic analysis was adjusted with the help of a Cambridge Instrument *p*H-meter with a glass electrode.

Standard globin solution was prepared from hemoglobin, dissolved in KOH, by the addition of 1.0*N*-HCl, when heme was precipitated as hemin. The concentration of globin solution, determined approximately from the difference in the weights of hemoglobin used and hemin obtained, was checked by Kjeldahl's method. Optical rotation of the globin solution was found ; and knowing the concentration, specific rotation of globin solution was determined, which was used to check the concentration of globin solution prepared for use from time to time. 1.0% Globin solution (40 c.c.) was used every time for the polarographic study.

Part I : *J. Univ. Bombay*, 1928, **26**, Part II, 15.

It was observed from polarographic measurements that the reaction between the metal ions and globin was slow. So the readings were taken from time to time and were found to be constant after 75 minutes in case of Co, Zn, and Ni and after 60 minutes in case of Cd. The constant values of diffusion currents of cobalt, nickel, zinc, and cadmium acetate solutions of various concentrations (0.0075—0.02*M*) in 0.1*N*-KCl as supporting electrolyte, with 0.01% globin as suppressor, at *p*H 5.0 and at 37° are shown in Table I and those with 1.0% globin in Table II, and at *p*H 6.6 in Tables III and IV for Zn and Cd respectively.

The factor, *F*, determined in Table I, was used in Table II for calculating the final concentration of the metal ions. The respective polarograms are shown in Figs. 1-6. μ_A = current in microamps; $E_{\frac{1}{2}}$ = half-wave potential of the metal ion *vs.* the Hg-pool; t = drop-time in secs; m = rate of flow of mercury in mg. sec^{-1}; D = diffusion coefficient = $(i_d/607nCm^{\frac{2}{3}}t^{\frac{1}{6}})^2$. In Table IV C_b is the max. value of $X = \frac{i_{d_0} - i_d}{F} \times \frac{40}{1000}$.

TABLE I

Metal ion.	Conc. (*C*).	Half-wave potential ($E_{\frac{1}{2}}$).	$mg.^{\frac{2}{3}}t^{\frac{1}{6}}$ ($mg.^{\frac{2}{3}}sec^{-\frac{1}{2}}$)	Diffusion current, i_{d_0}	Diffusion coeff. (*D*). ($cm^2.sec^{-1}$)	$i_d/C.$ (*F*) (μ_A/mol.)
Co^{2+}	0.0200*M*	−1.25volts	2.264	57.0 μ_A	1.038×10^{-6}	2850.0
	0.0150	−1.30	2.256	42.9	1.090×10^{-6}	2860.0
	0.0100	−1.30	2.240	28.4	1.091×10^{-6}	2840.0
	0.0075	−1.30	2.230	21.4	1.111×10^{-6}	2853.3
						Mean 2850.8
Ni^{2+}	0.0200	−1.10	2.288	54.4	0.959×10^{-6}	2720.0
	0.0150	−1.15	2.244	40.1	0.963×10^{-6}	2673.3
	0.0100	−1.15	2.233	26.9	0.993×10^{-6}	2690.0
	0.0075	−1.15	2.233	20.0	0971×10^{-6}	2666.7
						Mean 2687.5
Zn^{2+}	0.0200	−1.30	2.254	63.4	1.342×10^{-6}	3170.0
	0.0150	−1.30	2.237	47.3	1.349×10^{-6}	3153.3
	0.0100	−1.30	2.236	31.7	1.365×10^{-6}	3170.0
	0.0075	−1.30	2.226	23.8	1.380×10^{-6}	3173.3
						Mean 3166.7
Cd^{2+}	0.0200	−0.80	2.246	60.6	1.235×10^{-6}	3030.0
	0.0150	−0.80	2.238	45.3	1.236×10^{-6}	3020.0
	0.0100	−0.85	2.230	30.2	1.244×10^{-6}	3020.0
	0.0075	−0.85	2.228	22.7	1.252×10^{-6}	3026.0
						Mean 3024.2

TABLE II

Metal ion.	Initial conc. (in presence of 0.01% globin). (C).	i_{d_0}.	Half-wave potential ($E_{\frac{1}{2}}$).	Final conc. (in presence of 1.0% globin) (i_d).	Decrease in conc. of metal ion ($i_{d_0}-i_d$).	Amount of metal combined in g.atoms with 0.4g. of globin. (X) $\left[\frac{i_{d_0}-i_d}{F}\times\frac{40}{1000}\right]$	No. of atoms of the metal combined with one molecule of globin (Y) $\left[\frac{X\times 60,672}{0.40}\right]$
Co^{2+}	0.0200M	57.0μ_A	−1.30volts	45.8μ_A	11.2μ_A	1.549×10^{-4}	23.44
	0.0150	42.9	−1.35	31.7	11.2	1.549×10^{-4}	23.44
	0.0100	28.4	−1.35	17.3	11.1	1.535×10^{-4}	23.29
	0.0075	21.4	−1.35	10.4	11.0	1.522×10^{-4}	23.08
							Mean 23.31
Ni^{2+}	0.0200	54.4	−1.15	44.4	10.0	1.488×10^{-4}	22.58
	0.0150	40.1	−1.15	30.2	9.9	1.473×10^{-4}	22.36
	0.0100	26.9	−1.15	17.1	9.8	1.458×10^{-4}	22.13
	0.0075	20.0	−1.15	10.3	9.7	1.444×10^{-4}	22.91
							Mean 22.29
Zn^{2+}	0.0200	63.4	−1.30	51.0	12.4	1.566×10^{-4}	23.75
	0.0150	47.3	−1.30	34.9	12.4	1.566×10^{-4}	23.75
	0.0100	31.7	−1.30	19.5	12.2	1.541×10^{-4}	23.37
	0.0075	23.8	−1.30	11.8	12.0	1.516×10^{-4}	22.99
							Mean 23.47
Cd^{2+}	0.0200	60.6	−0.80	49.4	11.2	1.481×10^{-4}	22.48
	0.0150	45.3	−0.80	34.3	11.0	1.455×10^{-4}	22.08
	0.0100	30.2	−0.85	19.4	10.8	1.429×10^{-4}	21.67
	0.0075	22.7	−0.85	12.1	10.6	1.403×10^{-4}	21.27
							Mean 21.88

TABLE III

Metal ion.	Conc.	Half-wave potential.	$m^{\frac{2}{3}}t^{\frac{1}{3}}$. ($mg^{\frac{2}{3}}$. $sec^{-\frac{1}{2}}$)	Diffusion current. (i_{d_0})	Diff. coeff. (D) (cm^2. sec^{-1})	i_{d_0}/C. (F) (μ_A/mol.)
Zn^{2+}	0.0200M	−1.25volts	2.252	62.2μ_A	1.294×10^{-6}	3110.0
	0.0150	−1.30	2.239	47.0	1.329×10^{-6}	3133.0
	0.0100	−1.25	2.234	31.4	1.341×10^{-6}	3140.0
	0.0075	−1.25	2.226	23.6	1.356×10^{-6}	3147.0
						Mean 3132.5
Cd^{2+}	0.0200	−0.75	2.251	62.5	1.308×10^{-6}	3125.0
	0.0150	−0.80	2.245	47.0	1.322×10^{-6}	3133.0
	0.0100	−0.80	2.235	31.2	1.323×10^{-6}	3130.0
	0.0075	−0.80	2.230	23.6	1.344×10^{-6}	3133.0
						Mean 3130.5

TABLE IV

Metal ion.	Initial conc. (in presence of 0.01% globin).	i_{d_o}.	Half-wave potential.	Final conc. (in presence of 1.0% globin). (i_d)	Decrease in conc. of metal ion. (i_{d_o}-i_d)	Amount of metal combined in g. atoms with 0.4g. of globin. (X) $\left[\frac{i_{d_o}-i_d}{F}\times\frac{40}{1000}\right]$	No. of atoms of the metal combined with one molecule of globin. (Y) $\left[\frac{X\times 60,672}{0.40}\right]$	Degree of ionisation of the complex. (Z) $\frac{C_b-X}{C_b}$.
Zn^{2+}	0.0200*M*	62.2 μ_A	−1.3 volts	52.0 μ_A	10.2 μ_A	1.302×10^{-4}	19.76	0.000
	0.0150	47.0	−1.3	36.8	10.2	1.302×10^{-4}	19.76	0.000
	0.0100	31.4	−1.3	21.4	10.0	1.277×10^{-4}	19.37	0.017
	0.0075	23.6	−1.3	13.8	9.8	1.251×10^{-4}	18.99	0.037
							Mean 19.47	
Cd^{2+}	0.0200	62.5	−0.80	53.0	9.2	1.176×10^{-4}	17.84	0.096
	0.0150	47.0	−0.80	37.9	9.1	1.163×10^{-4}	17.64	0.105
	0.0100	31.2	−0.85	22.2	9.0	1.150×10^{-4}	17.45	0.115
	0.0075	23.5	−0.85	14.6	8.9	1.138×10^{-4}	17.26	0.125
							Mean 17.55	

DISCUSSION

Table I shows that the ratio of the diffusion current (i_{d_o}) to the molar concentration '*C*' is constant for a particular ion. This ratio (*F*) has been utilised to find the metal ion concentration in presence of globin. The value of the product $m^{\frac{2}{3}}t^{\frac{1}{4}}$ as shown in column 4 of Table I is also nearly constant at the different initial concentrations of the metal ions. This shows that the diffusion current in the electrolytic cell was regular for these concentrations and that the polarometer was working properly. On mixing a solution of globin with that of the acetate of the metal, Co, Ni, Zn or Cd, no precipitate was obtained even on centrifuging.

FIG. 1

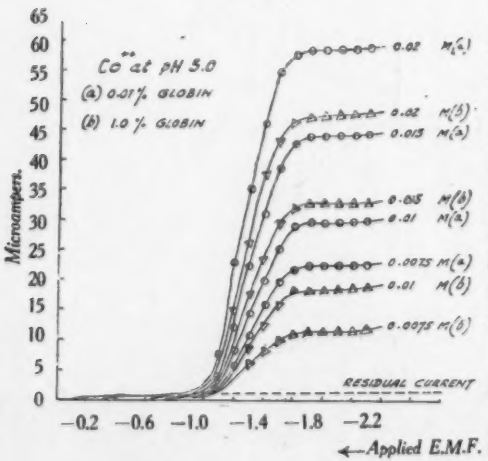
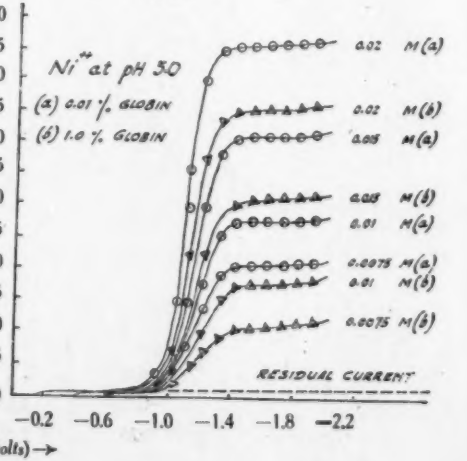


FIG. 2



Polarograms corresponding to Table II, recorded in Figs. 1-4 (*b*-curves) show that the diffusion currents of Co^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+} ions at *p*H 5.0 in presence of 1.0% globin are much less than those in case of 0.01% (*a*-curves). The diffusion current goes on decreasing and remains constant after 75 minutes in the case of Co^{2+}, Ni^{2+}, and Zn^{2+} and after 60 minutes in case of Cd^{2+} ions, when the reaction is supposed to be complete. The kinetics of the complex formation of Co^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+} ions at *p*H 5.0 have been studied and will be published in a separate communication. The difference in the values of diffusion currents in presence of of 0.01% and 1.0% globin leads to the conclusion that the metal ions are reacting with globin at *p*H 5.0. According to Tanford (*J. Amer. Chem. Soc.*, 1950, **72**, 441) the -COOH groups of protein ionise between *p*H 2.0 and 5.5. So in the above investigation at *p*H 5.0, the metal ions must have displaced the H atoms of the -COOH groups of globin. Maximum 24 atoms of a bivalent metal have been found to combine with one molecule of globin at *p*H 5.0 in case of Zn.

FIG. 3

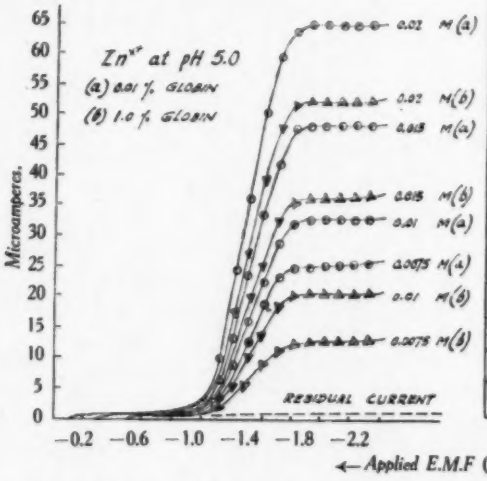
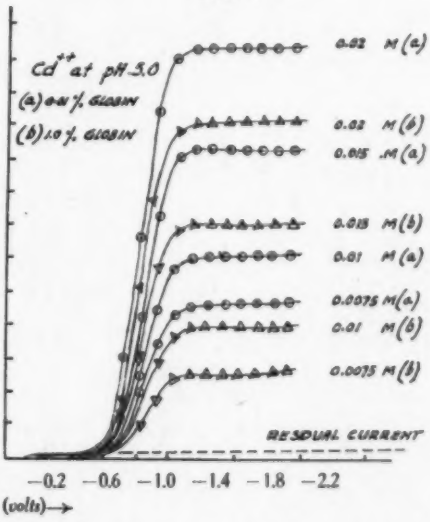


FIG. 4



Since a bivalent metal will combine at two monovalent groups of globin, which ionise at this *p*H, there must be maximum 48 such sites of combination. But according to Tristram (vide Roughton, "Chemistry and Biology of Proteins: Hemoglobin", Interscience Publishers Inc., New York, 1949, p. 109) there are 70 -COOH groups in 10^5g. of horse hemoglobin. So there are 48 -COOH groups in one molecule of hemoglobin (M.W. 68,000); subtracting from this 8 -COOH groups of 4 heme residues, one molecule of globin will contain 40 -COOH groups, which account for 20 atoms of the metal; the remaining 4 may be combining at 8 -SH groups since there are 8 atoms of sulphur in one molecule of globin. Again, it is observed that the lower the concentration of the metal ions, the less the combination; this may be due to the partial ionisation of the complex formed.

Polarograms recorded in Figs. 5 and 6 (*b*-curves) show that at *p*H 6.6 the diffusion currents of Zn^{2+} and Cd^{2+} ions in presence of 1.0% globin are less than that in case of 0.01%. It was observed that the diffusion currents in all cases went on decreasing with time and ultimately remained constant after 75 minutes in case of Zn and 60 minutes in case of Cd, thus indicating the gradual combination of Zn^{2+} and Cd^{2+} ions with globin at *p*H 6.6. The kinetics of the complex

formation of Co^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+} ions at *p*H 6.6 have been studied and will be published shortly.

FIG. 5

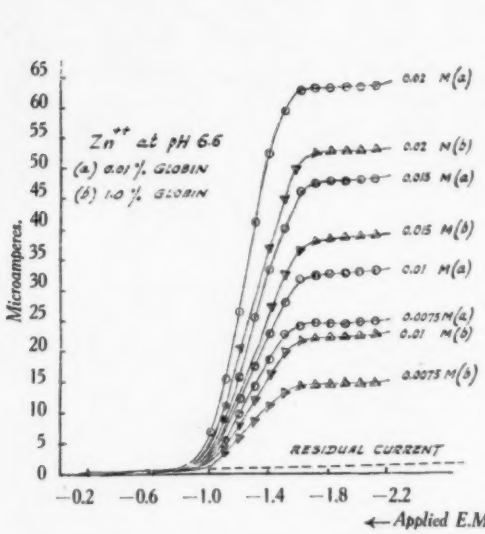
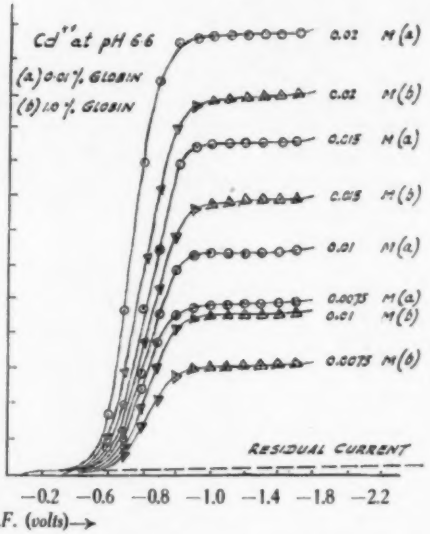


FIG. 6



←Applied E.M.F. (volts)→

According to Tanford (*loc. cit.*) the imidazole groups of proteins ionise between *p*H 6.0 and 8.0. So in the above investigation at *p*H 6.6, the metal ions must have combined at the imidazole groups of the histidine residues of globin. The identity of the groups on a protein molecule, which bind a species of a metal ion, can sometimes be inferred from the number of sites at which the metal is bound. In the present investigation the authors have found maximum 40 sites in one molecule of globin where metal atoms combine with it at *p*H 6.6 since Table IV shows that the maximum number of bivalent metal ions that can combine with a globin molecule is 20. The small difference in the number of combined atoms in the case of the two metals, Zn and Cd, and at different concentrations, is attributed to ionisation of the metal-protein complex, which is found to increase with dilution.

According to Tristram (*loc. cit.*) there are 56 imidazole groups in 10^5 g. of horse hemoglobin ; from this the number of histidine residues in one molecule of horse hemoglobin (M.W. 68,000), and hence in one molecule of globin, is calculated to be 38. Since the figure 40, determined by the authors by polarographic method, nearly tallies with the above figure 38, as determined by organic chemistry methods, it is concluded that at *p*H 6.6 the metals, Zn and Cd, must have combined with the imidazole groups of the histidine residues of globin. At *p*H 6.6 -COOH groups cannot be active to allow H to be replaced by a metal.

Though the above coincidence of results is observed, yet there can be a plea that the fall in diffusion current in presence of 1.0% globin may be due to decrease in diffusion coefficient owing to increase in viscosity. But it was observed by the authors that the diffusion current in presence of 1.0% globin decreased with time, reaching minimum after 75 minutes in case of Co, Ni, and Zn and 60 minutes in case of Cd ; in addition to this it was observed that the rate of fall in the diffusion current increased with the initial concentration of the metal ions. This fact supports the combination of the metal ions with the protein molecules.

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STUDIES ON THE PRECIPITATION OF THORIUM HYDROXIDE. PART II*. INTERACTION OF THORIUM CHLORIDE AND POTASSIUM HYDROXIDE

BY RAMESHWAR PRASAD AND ARUN K. DEY

A quantitative study of the association of potassium and chlorine ions with the precipitated material by the interaction of thorium chloride and potassium hydroxide solutions has been made. The precipitation of thorium hydroxide is complete with 3.6 equivalents of alkali when the concentration of thorium salt solution is 0.0625*M*, and 3.8 equivalents when the concentration is 0.0156*M*. In both the cases complete precipitation occurs in acidic medium. It has also been noted that the association of potassium ions has been found to increase, in general, with increase in the quantity of alkali added while that of chlorine diminishes under the same conditions. With increase in temperature and with higher dilution, the association of both ions diminishes.

It has been observed by the workers from these laboratories (vide Ghosh, *Proc. Indian Sci. Cong.*, Part II, *Chem. Sec.*, 1958) that the amount of alkali required for complete precipitation of a heavy metal hydroxide from its salt solution is always less than the theoretical amount. There is also an association of the corresponding anions with the precipitate which led Britton (*Ann. Rep. Chem. Soc.*, London, 1943, **40,** 44) to postulate the formation of basic salts in such precipitation phenomena.

Dey and Ghosh (this *Journal*, 1947, **24,** 181 ; 1950, **27,** 66 ; *Proc. Nat. Acad. Sci., India*, 1948, **17A,** 93) do not agree to the view of the formation of basic salts. They regard the presence of anion in the precipitate purely due to the adsorptive forces and that the adsorption of the anion results in the generation of free alkali, which in its turn completes the precipitation of the hydroxide. We have observed (*Vig. Pari. Anu. Patrika*, 1960, **3,** 155) that from a 0.0625*M* thorium chloride solution 3.6 equivalents of alkali are able to precipitate thorium completely from the solution.

In this communication observations have been recorded on the changes in the medium and the adsorption of ions, when thorium hydroxide is precipitated from its salt solution with potassium hydroxide.

EXPERIMENTAL

A solution of thorium chloride (BDH-LR) was prepared, and thorium and chloride ions were estimated by the usual methods ; the ratio of these ions was 1 : 4. A solution of potassium hydroxide was prepared from a BDH-AnalaR sample and it was standardised against acid using methyl red as an indicator. All other chemicals used were of the reagent grade.

Procedure.—In several 100 c.c. volumetric flasks 20 c.c. portions of standard thorium chloride solution were taken; varying amounts of KOH solution were added and the volumes raised to 100 c.c. in every case. The precipitates were allowed to settle overnight and the supernatant liquids were quantitatively analysed for H^+ or OH^- and Cl^- and K^+ ions.

* Part I : *Proc. Nat. Acad. Sci., India*, 1959, **28A,** 350.

For the estimation of acidity or alkalinity, an aliquot portion was titrated against a standard alkali or acid using methyl red as indicator. Chloride ion was estimated by titration against a standard silver nitrate solution using dichlorofluorescein as an adsorption indicator.

For the estimation of potassium ions, 10 c.c. of the supernatant liquid was diluted to 100 c.c. and the concentration of potassium determined with the help of a flame photometer (B. Lange, Model 5).

The experiments were performed at three different temperatures. The individual solutions and a bottle of water (used later for dilution) were kept in a thermostat maintained at a constant temperature (within $\pm$ 0.1°). The solutions were mixed and kept in the thermostat for 24 hours.

All concentrations in the following tables and figures are the final ones and are expressed in mg. *M* per litre.

TABLE I

H^+ *-ion concentration in the supernatant liquid.*

Conc. of $Th^{4+} = 50$ mg. ions. Conc. of $Cl^- = 200$ mg. ions.

Ratio $Th^{4+} : OH^-$.	Hydrogen ions (in mg. ions). 20°.	50°.	70°.
1:3.0	16.8	17.7	12.6
1:3.2	8.5	15.5	9.5
1:3.4	4.7	8.0	6.0
1:3.6	2.7	1.5	2.1

TABLE II

OH^- *-conc. in the supernatant liquid.*

Conc. of Th^{4+} and Cl^- same as in Table I.

Ratio $Th^{4+} : OH^-$.	Hydroxyl ions (in mg. ions). 20°.	50°.	70°.
1:3.8	0.2	0.6	0.8
1:4.0	0.5	1.0	1.1
1:4.2	7.3	8.5	9.1
1:4.4	18.0	19.7	19.7
1:4.6	29.0	31.2	32.2
1:4.8	39.0	42.0	42.3
1:5.0	51.0	51.2	55.0

The medium became just alkaline when 3.8 equivalents of the alkali were added, though thorium had already been precipitated completely at 3.6 equivalents.

It may be noted that thorium is precipitated in this case with 3.8 equivalents of alkali and the supernatant liquid is just alkaline when four equivalents of alkali are added to the system.

In order to economise space, the adsorption of potassium and chloride ions are represented graphically in Figs. 1 and 2, the observations being omitted.

TABLE III

H^+-ion conc. in the supernatant liquid.

Conc. of Th^{4+} = 12.5 mg. ions. Conc. of Cl^- = 50 mg. ions.

Ratio Th^{4+} : OH^-.	Hydrogen ions (in mg. ions). 20°.	50°.	70°.
1:3.0	4.6	5.0	5.0
1:3.2	3.6	2.9	2.8
1:3.4	0.8	0.8	0.8
1:3.6	0.4	0.3	0.2
1:3.8	0.1	0.1	0.1

TABLE IV

OH^- ion conc. in the supernatant liquid.

Conc. of Th^{4+} and Cl^- same as in Table III.

Ratio Th^{4+} : OH^-.	Hydrogen ions. (in mg ions). 20°.	50°.	70°.
1:4.0	0.3	0.4	0.5
1:4.2	2.2	2.3	2.4
1:4.4	5.2	5.2	5.2
1:4.6	7.8	8.3	8.8
1:4.8	10.6	11.0	11.5
1:5.0	13.3	14.1	14.5

DISCUSSION

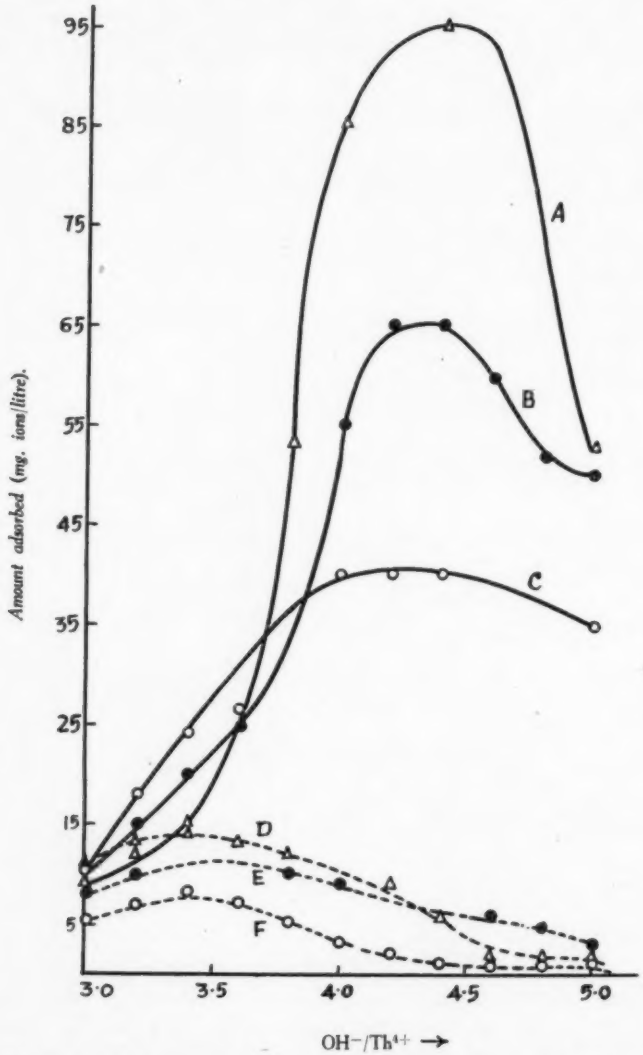
From the results it is noted that precipitation is complete while the alkali added is still in deficient quantity. The value approaches four equivalents when the precipitants used are dilute (Tables I—IV).

We observe that the association of potassium ions with the precipitate goes on increasing with increasing amounts of alkali to a point beyond four equivalents and then finally decreases (Figs. 1 and 2). At higher temperatures, however, the association has a tendency to decrease, probably

due to the decrease in the surface activity of the hydroxide. At the lower concentration the precipitation values approach the theoretical equivalent.

The association of chloride ions with the precipitate decreases with increasing quantity of alkali added. The first few points in Fig. 2 (curve E) do not agree to this because precipitation

FIG. 1



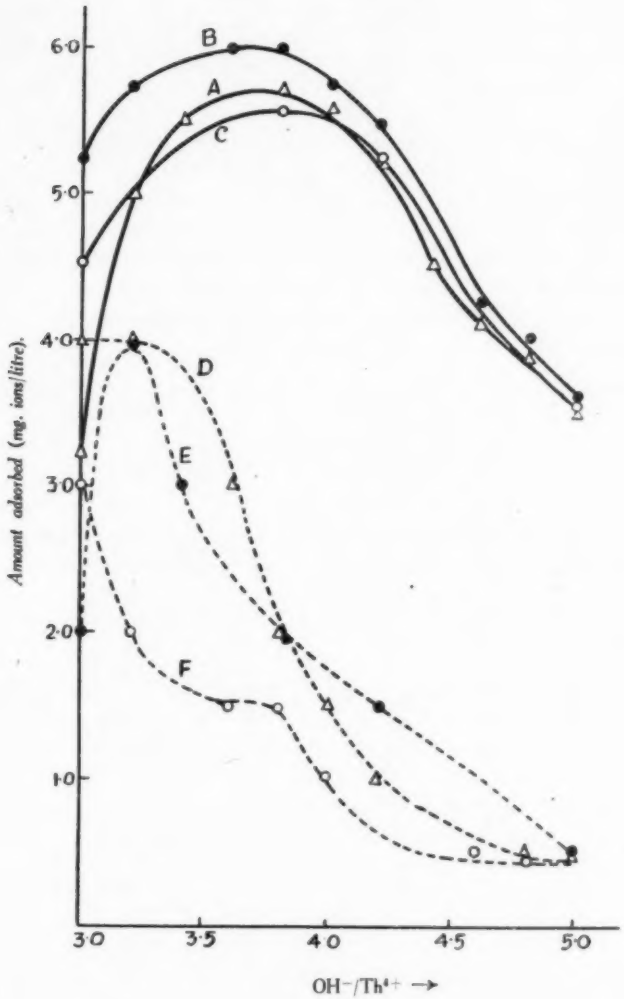
Adsorption of K^+ and Cl^- by the hydroxide, precipitated from 0.0625*M* thorium chloride (final conc.), by varying amounts of potassium hydroxide.

Solid lines represent the association of K^+ and broken lines that of Cl^-.

Curves: A 20°, B 50° and C 70°.

Curves: D 20°, E 50° and F 70°.

FIG. 2



Adsorption of K^+ and Cl^- by the hydroxide, precipitated from 0.0156 *M* thorium chloride (final conc.), by varying amounts of potassium hydroxide.

Solid lines represent the association of K^+ and broken lines that of Cl^-.

Curves: A 20°, B 50° and C 70°.
Curves: D 20°, E 50° and F 70°.

remains incomplete with the small amount of alkali added. The association of chloride ions, in general, diminishes with rise in temperature.

These observations are in accordance with a hypothesis advanced earlier from these laboratories (Dey and Ghosh, *Proc. Indian Sci. Cong.*, Part III, *Chem. Sec.*, 1951) on the behaviour of

hydroxides. According to the scheme, thorium hydroxide is precipitated by the interaction of thorium and hydroxyl ions. The hydroxide behaves as shown by the following equations:

$$Th(OH)_4 \rightleftharpoons Th(OH)_3^+ + OH^- \quad .. \quad .. \quad (i)$$
$$Th(OH)_3^+ \rightleftharpoons ThO_2 + H_2O + H^+ \quad .. \quad .. \quad (ii)$$
$$H^+ + OH^- \rightleftharpoons H_2O \quad .. \quad .. \quad .. \quad (iii)$$

Equation (*i*) shows the basic character of the hydroxide; this would explain the greater association of Cl^- ions in a medium, which is not alkaline. With increase in alkalinity the basic character would diminish and thus the association of chlorine with the precipitate would also diminish. Equation (*ii*) shows the liberation of a proton from the positively charged material $Th(OH)_3^+$. This liberation would be less improbable from $Th(OH)_4$, which is neutral. This is responsible for the acidic properties of the hydroxide, and thus the association of K^+ ions would be favoured as the concentration of alkali is increased. This is also evident from our experimental results.

In a predominantly alkaline medium, equation (*ii*) will be favoured, but at the same time would lead to the formation of an inert product, ThO_2, by the mutual interaction of the acidic and basic properties of the hydroxide, as shown by equation (*iii*), resulting in the liberation of water. Thus in the presence of an excess of alkali, the adsorptive capacity will diminish due to the growing inertness of the medium.

The authors express their gratitude to Prof. S. Ghosh and to the late Dr. S. P. Mitra for their interest in the work. They also thank the Council of Scientific and Industrial Research for supporting the work and for the grant of an assistantship to one of them (R.P.).

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PHOTOLYTIC SEPARATION OF URANIUM FROM VANADIUM

BY I. B. MISHRA, BALARAM SAHOO AND D. PATNAIK

The separation of uranium from vanadium has been carried out by photolysis in sunlight. For this purpose, solution mixtures of uranyl sulphate and vanadyl sulphate or ammonium vanadate, containing formic acid and ethanol, were exposed to sunlight. Pure uranium was precipitated in the form of the hydrated oxysulphate, leaving vanadium in solution. The influence of H^+-ion concentration, time period of exposure, and the percentage composition of ethanol on the recovery of uranium has been investigated.

Harris and Kolthoff (*J. Amer. Chem. Soc.*, 1945, **67**, 1484) isolated a compound of composition $UOSO_4$, $8H_2O$ by photolysis of uranyl sulphate in presence of excess of sulphuric acid and 40% ethanol on exposure to sunlight. While it took them several days for isolating their compound, Sahoo and Patnaik (this *Journal*, 1959, **36**, 483) readily obtained $UOSO_4$, $3.3H_2O$ on exposing a solution of uranyl sulphate in presence of formic acid and ethanol to sunlight. This fact clearly indicates that the compounds obtained by the two sets of workers are not the same. The compound, isolated by us under the conditions reported by Harris and Kolthoff (*loc. cit.*), on analysis provides, the formula $U(SO_4)_2$, $4H_2O$ and M.W. 502, as already reported by Meyer and Nachod (*Annalen*, 1924, **440**, 186).

This compound, when left in a desiccator for about a week, undergoes dehydration, producing the compound having M.W. 492 to which Harris and Kolthoff attributed the formula $UOSO_4$, $8H_2O$, and M.W. 494. As they were interested in the polarographic determination of uranium, obviously they did not ascertain the exact composition of the compound isolated by them since uranium to sulphate ratio was not mentioned.

This photolytic isolation of the $UOSO_4$, $3.3H_2O$ has been adopted for the separation of uranium from vanadium. While ethanol has been used as the reducing agent, as also for the purpose of precipitation, formic acid serves the purpose of maintaining the required *p*H in preventing hydrolysis and also of a reducing agent. The yield and purity of uranium recovered by the method depend on such factors like variation of *p*H, the period of exposure to sunlight, the ratio of uranium to vanadium, and the percentage composition of ethanol in the solution. These factors within wide range of variation have been investigated.

EXPERIMENTAL

Uranyl nitrate and vanadyl sulphate of E. Merck E.P. quality, and ammonium vanadate of B.D.H. quality were used. Uranyl sulphate was prepared from the nitrate and was made free of the mineral acid. Stock solutions of uranium and vanadium salts containing small amounts of formic acid to prevent hydrolysis were used. Solution mixtures of uranyl sulphate and ammonium vanadate or vanadyl sulphate of known U_3O_8 and V_2O_5 content were prepared. To this mixture formic acid was added to bring the solution to required *p*H, after which ethanol was added to have the necessary ethanolic composition. The total volume of the solution was always 100 c.c. The solutions were then exposed to sunlight when uranium was precipitated as the hydrated oxysulphate. After the required period of exposure, the precipitate was filtered, washed, and analysed for the recovery and purity of uranium as reported previously (Singh, Sahoo and Patnaik, *Proc. Ind. Acad. Sci.*, 1959, **50A**, 129). Vanadium was analysed colorimetrically (Sandell, "Colorimetric Determination of Traces of Metals", Vol III, pp. 443-44, Interscience Publishers, Inc., New York).

Gopala Rao *et al.* (*Z. anal. Chem.*, 1956, **150**, 178) found that exposure of an hour to bright sunlight was sufficient for the reduction of uranium (VI) to uranium (IV) present as sulphate in H_2SO_4 (dil.) with ethanol. Presence of vanadium was found to require enhanced period of exposure. From Table I it appears that the recovery of uranium increases with the increase in the period of exposure for a 40% ethanolic composition of *p*H 2.1-2.3, U_3O_8 to V_2O_5 ratio being 500.1 to 153.4 and 500.1 to 225.1. The increase of vanadium ratio in the mixture appears also to diminish the percentage recovery of uranium under similar conditions. Duration of exposure for at least 15 hours is therefore considered necessary for the usual vanadium content, associated with uranium. It can also be found in the same table that when the *p*H is 2.1-2.3, percentage of recovery of uranium is always more than that when the *p*H is 1. It has been found, however, that the uranium obtained at *p*H 3 and above is contaminated with vanadium.

TABLE I

40 % Ethanol composition by volume.

Comp. of the mixture calc. as oxides. U_3O_8.	V_2O_5.	*p*H.	%Recovery of uranium with period of exposure for 2 Hrs.	4 Hrs.	15 Hrs.
500.1 mg.	153.4 mg.	1.0	33.94	45.60	82.72
,,	,,	2.1—2.3	39.88	76.74	90.68
,,	225.1	1.0	8.56	10.68	53.96
,,	,,	2.1—2.3	19.32	49.88	63.52

A series of mixtures, having different alcoholic compositions by volume, within the *p*H range 2.1 to 2.3 was next exposed to sunlight to study the influence of alcohol. The data recorded in Table II show that the recovery of uranium is influenced by the composition of alcohol. The yield increases very appreciably with increase of alcohol composition up to 40% after which the yield diminishes. At 40% ethanolic composition the recovery is about 92% while at 60% ethanol it is about 96%.

TABLE II

Comp. of the mixture calc. as oxides. U_3O_8.	V_2O_5.	%Comp. of EtOH.	Uranium reovered estimated as U_3O_8 by Ignition.	Jones reductor.	%Recovery.
454.0 mg.	98.15 mg.	10	117.6 mg.	117.0 mg.	25.90
,,	,,	20	326.6	325.0	71.93
,,	,,	30	380.8	380.5	83.87
,,	,,	40	416.4	415.8	91.70
,,	,,	50	426.8	424.6	93.99
,,	,,	60	434.4	433.3	95.68

This photochemical process has been applied to the separation of uranium from a number of elements including rare-earths and thorium, which will be published in due course.

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BEHAVIOUR OF PERSULPHATE IN SULPHURIC ACID SOLUTIONS

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Behaviour of persulphate in sulphuric acid solution of different concentrations has been studied by estimating its hydrolytic products, permonosulphuric acid and hydrogen peroxide. The method of estimation of these substances in presence of each other works well and the difficulty encountered by the previous workers has been solved. It is confirmed that first permonosulphuric acid and then hydrogen peroxide are formed as the concentration of sulphuric acid is increased. The graphical results show that there are two maxima for permonosulphuric acid and one for hydrogen peroxide. The second maximum for permonosulphuric acid proves that it is reformed at higher concentrations of sulphuric acid. The reaction between hydrogen peroxide and sulphuric acid has also been studied. The possibility of estimating persulphate in suitable concentrations of sulphuric acid, iodometrically and with permanganate, has been indicated. The results are slightly different if the mixing of the reactants is reversed.

Persulphate or perdisulphuric acid is known to hydrolyse first to permonosulphuric acid and then to hydrogen peroxide in sulphuric acid solutions. Elbs and Schönherr (*Z. Elektrochem.* 1895, **1,** 417, 468) found the hydrolysis to increase with the increasing concentration of sulphuric acid. Palme (*Z. anorg. Chem.*, 1920, **112,** 97) calculated the rate constants for the two reactions, which were found to be unimolecular:

$$H_2S_2O_8 + H_2O \longrightarrow H_2SO_5 + H_2SO_4 \quad .. \quad (a)$$

$$H_2SO_5 + H_2O \rightleftharpoons H_2O_2 + H_2SO_4 \quad .. \quad (b)$$

Ahrle (*Z. angew. Chem.*, 1909, **22,** 1713) studied the rate of hydrolysis of Caro's acid to hydrogen peroxide and measured the equilibrium constant for reaction (*b*). Based on these observations standard methods were developed for the preparation of permonosulphuric acid either by the hydrolysis of potassium persulphate (Caro, *ibid.*, 1898, **11,** 845) or by the action of chlorosulphonic acid on hydrogen peroxide (d'Ans and Friederich, *Z. anorg. Chem.*, 1910, **43,** 1880) at low temperatures, pointing to the reversible nature of reaction (*b*). Several workers investigated the decomposition of persulphate at higher temperatures (70° or above) and some, in sulphuric acid solutions of low concentration. The product of decomposition is oxygen, and the mechanism of the process is different from the reactions (*a*) and (*b*) in both neutral or acid solutions because these reactions take place in high concentrations of sulphuric acid. Recently Szabo *et al.* (*Z. anorg. allgem. Chem.*, 1956, **287,** 152) have investigated the decomposition of persulphate in sulphuric acid solution, catalysed by metal ions.

In the present communication a detailed study of these reactions has been made by employing a wide range of concentration of sulphuric acid whereby not only the results of previous workers are confirmed but some additional interesting observations have also been made. The reaction (*a*) and probably the forward reaction (*b*) are slow, but a kinetic study of these in high concentrations of sulphuric acid could not be made because the mixing of sulphuric acid raises the temperature of the reaction mixture to a great extent. The results show only a qualitative behaviour of persulphate in sulphuric acid solutions of different concentrations.

There has always been a problem to estimate the persulphate and its hydrolytic products in presence of each other. The method of Palme (*loc. cit.*), though fairly suitable, is time consuming, requiring three determinations, one of which is indirect. Ceriometric determination of these compounds in presence of each other, as recommended by Csanyi and Solymosi (*Z. anal. Chem.*, 1954, **142,** 423) also could not be employed in the present investigation because it requires heating and adjustment of the acidity of the solutions, factors both of which would influence reactions (*a*) and (*b*). In the present case it was possible to estimate the persulphate, hydrogen peroxide, and permonosulphuric acid by making two determinations, viz., iodometry in dilute solutions of potassium iodide, and the titration with the permanganate. The latter was found to be quite suitable for the estimation of hydrogen peroxide. The presence of perdisulphuric acid does not interfere if the concentration of sulphuric acid is low and the titration is quickly carried out.

It has been found, however, that perdisulphuric acid either does not exist or does so only in very small concentration in presence of hydrogen peroxide. The possibility of a reaction between hydrogen peroxide and perdisulphuric acid therefore does not arise. The presence of permonosulphuric acid is also without any interference, as reported by Baeyer and Villiger (*Ber.*, 1900, **33,** 2488). No manganaous sulphate was added as sulphuric acid was quite sufficient for the purpose although the titration was attended with an induction period, depending on the acid concentration. In the present case the burette reading, for which the pink colour persisted for 5 to 10 seconds, was recorded. Some difficulty was encountered while titrating solutions containing a small amount of hydrogen peroxide and a large amount of permonosulphuric acid, but there was no difficulty at all in high sulphuric acid medium or when a large quantity of hydrogen peroxide was present. For iodometric determinations 10 c.c. of *N*/50 potassium iodide was mixed with the reaction mixture. A preliminary study indicated that permonosulphuric acid quantitatively liberated iodine from such solutions of potassium iodide, whereas hydrogen peroxide did so in about 10 to 15 minutes if the acid concentration was normal or above. Dilute solutions of persulphate will liberate negligible amounts of iodine from such solutions even in 15 minutes if the concentration of sulphuric acid is lower than one normal. The reaction mixture was added to potassium iodide solution and it was quickly titrated against a solution of sodium thiosulphate. This titrated solution was then kept for about 15 minutes and again titrated against thiosulphate. The method of calculation has been shown later.

EXPERIMENTAL

The potassium persulphate used was of E. Merck 'pro analysi' quality and sulphuric acid was of A.R. quality (sp. gr. 1.84) from Orient Scientific Industries, Agra. All other chemicals used were of B.D.H.-A.R. quality. Persulphate solutions were always freshly prepared by direct weighing and their concentrations were checked by arsenite (Gupta and Ghosh, *Anal.Chim.Acta*, 1957, **17,** 379) or Eckardt's method (*Chem. News*, 1900, **81,** 38).

Requisite quantities of distilled water and H_2SO_4(conc.) were taken in 500 c.c. conical flasks to obtain the desired concentrations of the acid in 50 c.c. solutions. The volume of the distilled water together with that of the acid in each flask was 40 c.c. Finally 10 c.c. of 0.1*N* persulphate solution was added. A 5 c.c. sample was taken out after an hour, diluted, and estimated for hydrogen peroxide with 0.01*N*-$KMnO_4$. Another 5 c.c. sample was diluted, added to 10 c.c. of *N*/50-KI containing a little starch solution, and quickly titrated against 0.01*N* sodium thiosulphate. This was then kept for about 15 minutes and again titrated for the liberated iodine. Tetrathionate made no complication. Dilution also had no effect on reaction (*a*) or (*b*). On the other hand, it helps check the reactions. 0.05*N* Persulphate (10 c.c.) was also used to note the effect of concentration.

The experiments were repeated by taking first distilled water and persulphate solution in the conical flask, and then adding H_2SO_4. Experiments were also performed with H_2O_2 (10 c.c. of 0.1*N* and 0.05*N*) and different concentrations of H_2SO_4.

Calculation of the Concentrations

At lower concentrations (below 3.6*M*) of H_2SO_4, when no H_2O_2 is present, the first quick iodometric titration estimates the permonosulphuric acid. The original oxidant (persulphate) minus this estimation furnishes the concentration of perdisulphuric acid.

In slightly higher concentrations (3.6 to 4.5 *M*) of the acid, when a small amount of hydrogen peroxide is also present, the first quick iodometric titration gives permonosulphuric acid as above and the second iodometric titration gives both H_2O_2 and permonosulphuric acid, and hence perdisulphuric acid can again be calculated.

At higher concentrations of the acid no perdisulphuric acid is present because the second iodometric titration gives the total oxidant equivalent to original persulphate.

The concentration of permonosulphuric acid can now be calculated by subtracting the concentration of H_2O_2 (determined by the permanganate) from the total oxidant (second iodometric titration). The first iodometric titration no longer gives permonosulphuric acid alone. A part of the liberated iodine is due to H_2O_2. In fact, the liberation of iodine from potassium iodide for the first quick titration depends on the concentrations of (1) permonosulphuric acid, (2) hydrogen peroxide, and (3) sulphuric acid. Hence as the amounts of H_2O_2 and H_2SO_4 increase in the mixture, much more iodine is liberated than what is expected from permonosulphuric acid alone.

A comparative study of these first iodometric titrations of different mixtures, however, indicates qualitatively whether the concentration of permonosulphuric acid is increasing or decreasing. At still higher concentrations of the acid, the total oxidant, as estimated by the second iodometric titration, also becomes less. This estimated total oxidant, subtracted from the initial oxidant, provides the amount of oxygen, the decomposition product of H_2O_2.

The reaction mixtures were always qualitatively tested for the presence or otherwise of H_2O_2 by titanium sulphate (Vogel, "A Textbook of Macro and Semimicro Qualitative Analysis", 1959, p. 599) and of perdisulphuric acid by a 2% acetic acid solution of benzidine (*ibid.*, 1959, p. 380). In order to make the latter test, the sulphuric acid of the mixture was first neutralised by solid sodium carbonate before adding benzidine solution.

TABLE I

Volume of the reaction mixture = 50 c.c. Reaction mixture titrated each time = 5 c.c. $K_2S_2O_8$ taken=10 c.c. of 0.1*N*

Overall conc. of H_2SO_4.	0.01*N*-$KMnO_4$ required (c.c.) after				0.01 *N*-Thiosulphate (c.c.) required after							
	1hr.	1day.	2days.	3days.	1hr.		1day.		2days.		3days.	
					1st.	2nd.	1st.	2nd.	1st.	2nd.	1st.	2nd.
3.6*M*	0	0	0	0	2.65	..	8.00	..	9.35	..	9.95	..
4.5	0	0.05	0.10	1.10	5.80	..	10.15	..	10.10	..	9.40	10.50
5.4	0	1.15	2.05	3.10	9.75	10.30	9.40	10.60	8.50	10.60	7.45	10.55
6.3	2.85	4.30	5.85	7.40	8.90	10.60	6.60	10.60	5.10	10.60	4.00	10.50
7.2	7.85	9.15	9.55	9.55	3.65	10.60	2.60	10.60	2.10	10.40	1.85	10.15
8.1	9.40	9.55	9.45	9.30	2.85	10.60	3.50	10.50	2.70	10.40	3.25	10.00
9.0	8.35	8.25	8.00	7.60	5.50	10.10	4.40	9.90	4.45	9.60	4.10	9.10
9.9	6.80	6.10	5.80	5.05	5.20	9.00	5.05	8.25	3.25	7.80	3.95	6.95
10.8	4.85	4.40	4.00	3.75	3.70	7.40	3.35	7.10	3.20	6.65	2.85	6.05
12.6	1.20	0.95	0.90	0.85	2.65	3.70	2.30	3.20	2.00	2.70	1.70	2.35

N.B. 1st and 2nd refer to the iodometric titrations, immediately and after 15 minutes respectively.

Considering the observations at 4.5*M* of H_2SO_4 (Table I), 5.80 c.c. gives permonosulphuric acid and 10.60-5.80=4.80 c.c. is the concentration of the remaining persulphate or perdisulphuric acid. After 3 days, 1.10 c.c. gives H_2O_2 and 9.40 c.c. gives permonosulphuric acid. The second iodometric titration value is 10.50 ; hence perdisulphuric acid is equal to 10.60-10.50=0.10 c.c. of thiosulphate, and there is no oxygen.

At 5.40*M* acid concentration after 3 days, 3.10 c.c. is H_2O_2 and 7.45 c.c. is permonosulphuric acid. Oxygen is equivalent to 10.60-10.55=0.05 c.c. of the thiosulphate, and there is no perdisulphuric acid. That 0.05 c.c. is oxygen and not perdisulphuric acid, easily follows from the fact that the second iodometric titration value increases and then decreases as the reaction progresses.

DISCUSSION

A typical set of results is shown in Table I. Figures 3 and 4 correspond to the results on the first and the fourth day of this table. Similar types of figures were obtained for the results of second and third day. Some of the results are shown in Figs. 1—8.

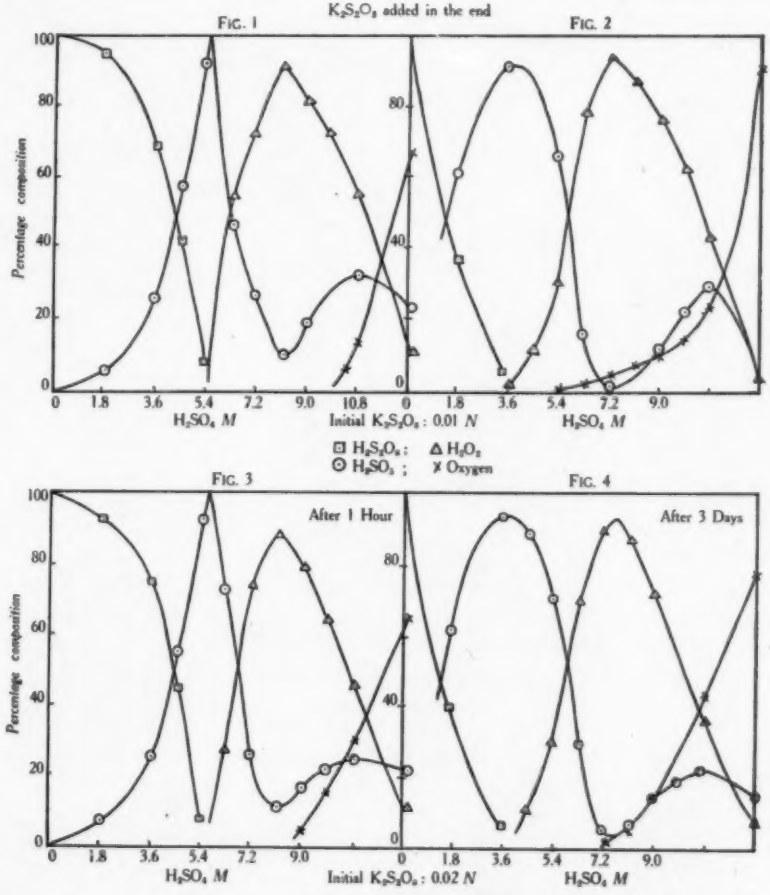
It may be seen from Figs. 1 to 4 that from persulphate or perdisulphuric acid, successively permonosulphuric acid and hydrogen peroxide are formed, and finally the latter decomposes, giving off oxygen. As the concentration of H_2SO_4 is increased, the amount of permonosulphuric acid increases, attains a maximum, then decreases, and increases again finally to decrease. This is easily inferred from the figures where there are two maxima for permonosulphuric acid. There is only one maximum for H_2O_2. It appears therefore that first permonosulphuric acid is formed from perdisulphuric acid.

$H_2S_2O_8 + H_2O \rightarrow H_2SO_5 + H_2SO_4$ .. (1) (approx. between 1.8 and 5.4*M* of H_2SO_4)
Permonosulphuric acid gives hydrogen peroxide:

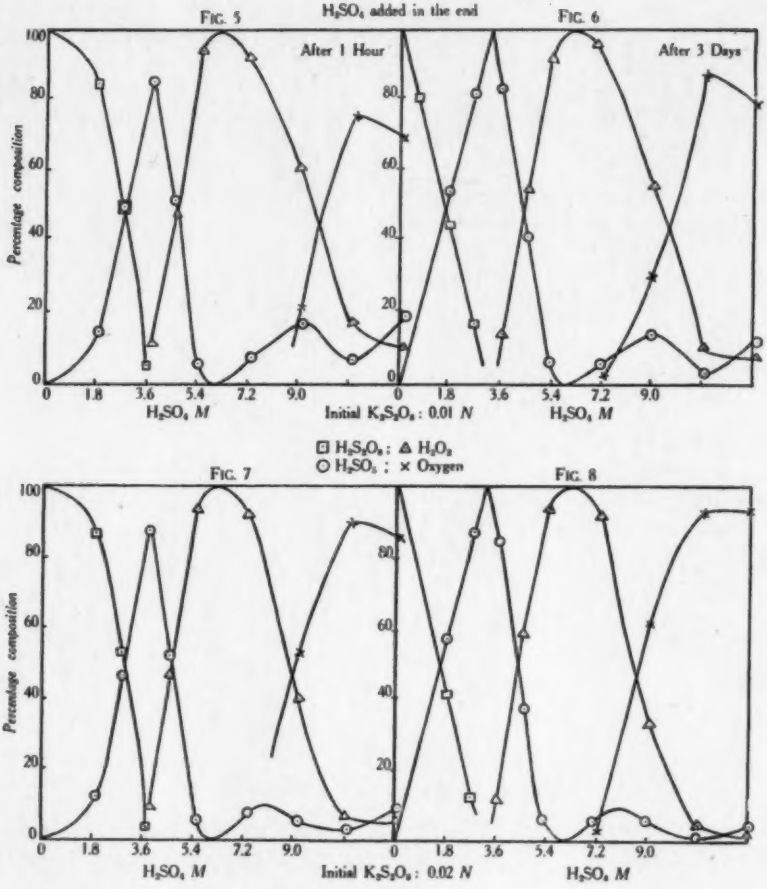
$H_2SO_5 + H_2O \rightarrow H_2O_2 + H_2SO_4$ .. (2) (predominantly between 5.4 and 8.1*M* of H_2SO_4)
Hydrogen peroxide is then used up in two ways. It reacts with sulphuric acid reproducing permonosulphuric acid :

$H_2O_2 + H_2SO_4 \rightarrow H_2SO_5 + H_2O$ .. (3) (between 8.1 and 10.8*M* of H_2SO_4)
Secondly hydrogen peroxide decomposes according as

$H_2O_2 \rightarrow H_2O + \frac{1}{2} O_2$ .. (4)



The decomposition is rapid and, in fact, very rapid in 12.6*M*-H_2SO_4 or above. It also takes place at lower concentrations of the acid, but only after 3 days. Thus there are two alternative reaction paths for hydrogen peroxide. At one stage reaction (3) predominates, but at higher



concentrations of sulphuric acid reaction (4) predominates. This explains the second maximum for permonosulphuric acid as also the decrease in the concentration of H_2O_2. At high concentrations of H_2SO_4, the lesser concentration of permonosulphuric acid is attributed not to its decomposition, but to the fact that its formation by reaction (3) is less in presence of predominating reaction (4).

The reaction of H_2O_2 with H_2SO_4 (relevant figures not shown) proves that reaction (2) is reversible, *i.e.*,

$$H_2SO_5 + H_2O \rightleftharpoons H_2O_2 + H_2SO_4 \qquad .. \quad (5)$$

The formation of permonosulphuric acid begins at about 8.1*M* concentration of H_2SO_4 and at very high acid concentration, its formation is less due to decomposition of H_2O_2.

The observations have been recorded also at intervals of 24, 48 and 72 hours. All the reactions are shifted to right with time. The effect of time is not well observed in case of reaction (3) because of the predominating reaction (4), which decreases the concentration of hydrogen peroxide.

The experiments were also carried out by adding H_2SO_4 in the last. The results are shown in Figs. 5 to 8. These differ from other results in so far that the reactions (1), (2), and (3) take place within lower limits of concentration of H_2SO_4. The addition of H_2SO_4 liberates much heat, which quite obviously increases the rates of all the reactions. It may also be mentioned that a fraction of persulphate decomposes by this heat, giving probably oxygen in such cases because the total oxidant estimated iodometrically (second titration) is somewhat always less than the original concentration of persulphate. No such complications are involved when the persulphate is mixed after addition of H_2SO_4 and the solution is cooled. It is not clear why the amount of permonosulphuric acid increases for the third time in about 12.6 *M*-H_2SO_4 (Figs. 5 to 8).

In the reaction H_2O_2-H_2SO_4, when sulphuric acid, instead of the peroxide, is added in the last, permonosulphuric acid is never present in large amount; in fact it is much less than in its parallel case when the peroxide is added in the last. The decomposition of H_2O_2 by the heat produced by the mixing of H_2SO_4 seems to be the reason again (relevant figures not shown).

The second maximum for permonosulphuric acid never goes high in any case, showing thereby that not much permonosulphuric acid is produced from reaction (3). This reaction is favourable in only very strong acid solutions, when unfortunately a rapid decomposition of H_2O_2 takes place. The reaction H_2O_2-H_2SO_4 (adding H_2O_2 in the last) was studied with higher concentrations (*N* and 2*N*) of H_2O_2 in about 15*M*-H_2SO_4 solution, when H_2O_2 decomposed, and no permonosulphuric acid was formed. The usual method for the preparation of permonosulphuric acid from chlorosulphonic acid and hydrogen peroxide is possible probably because it is carried out at low temperatures or because chlorosulphonic acid has very little decomposing action on H_2O_2.

Two interesting observations have been made which lead to the possibility of a quantitative determination of persulphate. From Figs. 5 to 8 it may be seen that in about 5.94*M* acid solution, the whole of the persulphate is present in the form of H_2O_2, which may be titrated against the permanganate. No such possibility is seen from Figs. 1 to 4 where the persulphate is added in the last. A separate communication has been made elsewhere for such an estimation. Similarly a possibility of estimating persulphate iodometrically in about 5.4*M* acid solutions is apparent from Figs. 1 to 4. Work is in progress to prepare permonosulphuric acid at ordinary temperatures by a simple method and to stabilise it.

Gupta and Ghosh (this *Journal*, 1958, **35,** 483) have reported that no red trivalent manganese is formed in 5.4*M*-H_2SO_4 solution because hydrogen peroxide produced in the system reacts with Mn(III). In the present investigation very little H_2O_2 is formed in such solutions (Figs. 1-4). Qualitative test for H_2O_2 with titanium sulphate, employed by Gupta and Ghosh (*loc. cit.*), might be misleading. When titanium sulphate prepared in H_2SO_4(conc.) is added to the reaction mixture, the high concentration of the acid of titanium sulphate solution produces H_2O_2, which responds to the test. In order to make this test in such solutions, a drop or two of the test solution should always be added to about 2 c.c. of the reaction mixture. Hence it is believed that Mn(III) is not formed because permonosulphuric acid, which is predominantly present in 5.4*M* acid solutions, probably does not oxidise Mn(II). Gupta and Ghosh (*ibid.*, 1959, **36,** 237) have also reported that Caro's acid does not oxidise Mn(II). The anticatalytic action of Mn(II) in the oxidation of oxalate (Gupta and Ghosh, *J. Inorg. Nucl. Chem.*, 1959, **11,** 320), and arsenious (Gupta, this *Journal*, 1959, **36,** 643; Gupta and Misra, *Bull. Chem. Soc., Japan*, 1959, **32,** 1306) and formic (Gupta amd Nigam, this *Journal*, 1960, **37,** 125) acids by persulphate can now be attributed to the formation of permonosulphuric acid, which probably does not oxidise the above acids. All these acids are, however, oxidised by the persulphate, a process which takes place by a free radical mechanism. The formation of permonosulphuric acid is catalysed by Mn(II), as has been reported

by Szabo *et al.* (*loc. cit.*). The results of the present investigation further explain the observation of Gupta and Ghosh (*Naturwiss.*, 1958, **45**, 184) as to why Mn(III) is formed only between the concentration limits of 3.6 to 5.4*M* of sulphuric acid. The most favourable concentration is 3.6 *M*, above which Caro's acid begins to be formed and below which there is insufficient sulphuric acid to hold Mn(III) in solution.

The results are fairly reproducible if care is taken to take exactly identical volumes of H_2SO_4 (conc.) in each case. While carrying out experiments to note the effect of concentration of persulphate, equal volumes of persulphate solutions of different concentrations should be added. It is not only the overall acid concentration that matters, but also the concentration of the acid in the solution to which persulphate is added, and which therefore should be identical in all cases for noting the effect of concentration of persulphate. In the other case, when sulphuric acid is added in the last, the reproducibility is less due evidently to the mode of mixing of sulphuric acid having some influence. If the mixing is standardised, say, by adding 0.5 c.c. at a time, the results do not deviate by more than 5 to 10%.

It may also be mentioned that if 100 c.c. or 25 c.c. solutions of reaction mixture are prepared instead of 50 c.c., no identical results are obtained. A volume contraction of 5 to 7% also took place by mixing of sulphuric acid with water or the persulphate solution, and this was taken into consideration while calculating the concentrations of different species in the reaction mixture.

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CHROMATOGRAPHIC STUDY OF ANIONIC COMPLEXES. PART VII. SEPARATION OF SOME IONS IN PRESENCE OF CITRATE USING AQUEOUS METHANOL AS SOLVENT

By Eric John Singh and Arun K. Dey

An attempt has been made to separate copper(II), cadmium (II), iron(III), nickel(II), and cobalt(II) from binary, ternary, quaternary, and pentanary mixtures by filter paper chromatography, using aqueous methanol as solvent. The effect of adding varying concentrations of citrate as a complexing agent to the solution has been studied.

In general, when two metals are present, the separation is effected up to the addition of nearly one equivalent of the complexing agent (ratio of total metal : citrate = 1:1). With higher concentration of the complexing agent, no sharp separation occurs. When three metals are present, less citrate is required for good separation. When four or more metals are in the mixture, the concentration of citrate varies for good separation.

In previous publications Singh and Dey studied the chromatographic separation of various metal ions in the presence of tartrate as complexing agent, using aqueous ethanol and methanol as solvent (*J. Chromatog.*, 1960, **3**, 146; this *Journal*, 1960, **37**, 235). We have extended now the work to some mixtures of ions and have attempted to employ complex-formation with citrate for the separation of ions by filter paper strip chromatography, using aqueous methanol as solvent.

Experimental

Solutions of sulphates of copper, nickel, cobalt, iron (III), and cadmium and of sodium citrate were prepared using reagent grade chemicals and standardised as usual. The arrangement for chromatography was that described by Gage *et al.* (*J. Chem. Ed.*, 1950, **27**, 159). Series of mixtures were prepared by taking equal concentrations of metals and adding varying quantities of sodium citrate solution, keeping the total volume constant. The equivalents of citrate mentioned in the figures and the description represent the ratio of total concentration of metals (obtained by adding the concentrations of metal in molarity) to the concentration of citrate added. After trials with varying concentrations of aqueous methanol, 50% methanol was found to effect good separation. The mixtures were spotted on Whatman filter paper No. 1 and the chromatograms were run at a constant temperature in a temperature-controlled room at 26°. The time allowed for movement of ions was 90 minutes. In binary, ternary, quaternary, and pentanary mixtures the final concentration of each of the metal ions was 0.05*M*, 0.042*M*, 0.031*M*, and 0.025*M* respectively. To ascertain the occurrence of good separation of the ions, the R_L and R_T values were determined. The data are recorded in Figs. 1 to 3, showing the variation of the R values with the concentration of citrate employed in some typical cases.

In the following mixtures, a solution containing $K_4Fe(CN)_6$ and H_2S was used for developing in all the cases except in mixtures containing nickel, where dimethylglyoxime was also used.

Separation of Nickel (II) *and Copper* (II).—The separation of the ions was possible up to 0.4 equiv. of citrate added; with higher concentrations of citrate no satisfactory separation was effected.

Separation of Copper (II) *and Iron* (III).—$K_4Fe(CN)_6$ was used for developing. The separation of Cu(II) and Fe(III) ions was possible up to one equivalent of citrate added; with higher concentrations of the same no separation was possible. In case of iron (III) tailing occurred up to 0.2 equivalent of citrate added; on increasing the concentrations of the same, tailing was reduced, and finally the R_T value became constant with 0.8 equiv. of citrate added.

Separation of Nickel(II) *and Iron* (III).—The separation of ions was effected up to 1.3 equiv. of citrate added. When the ratio of metal : concentration of citrate was 1:1.3 to 1:1.5, there was no sharp separation of the ions; with a ratio of 1:1.6 and above, no separation of the ions was possible.

Separation of Cobalt (II) *and Iron* (III).—The separation of ions was possible up to the addition of 1.5 equiv. of the complexing agent; with higher concentrations of the same, no separation was effected.

Separation of Copper (II) *and Cobalt*(II).—The separation of ions was effected up to the addition of 0.8 equiv. of the complexing agent; with higher concentrations of the same, no separation was possible. The *R* values of copper (II) became constant with 0.4 equiv. of the complexing agent added.

Separation of Copper(II) *and Cadmium*(II).—A good separation of the ions took place with ratios 1:1 to 1:3 equiv. of the complexing agent added. With a ratio of 1:1 or above, cadmium (II) ions did not move, only copper (II) ions moved upwards.

FIG. 1

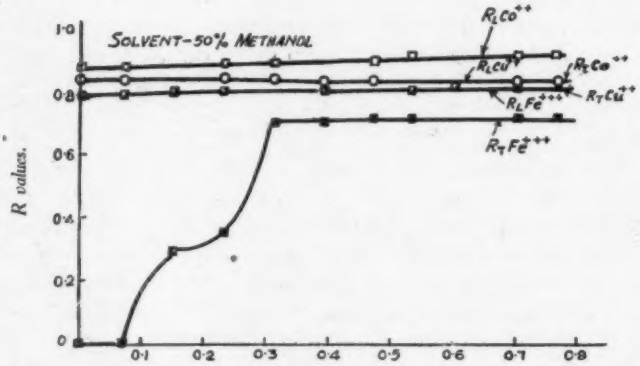
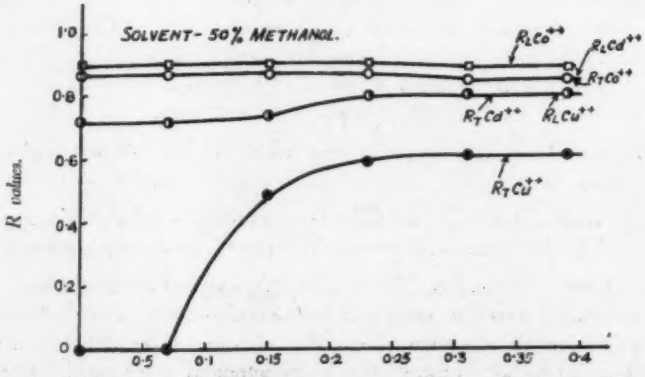


FIG. 2



Equivalents of sod. cit.

Separation of Cadmium (II) *and Iron* (III).—In the beginning no precipitation occurred. When about 3 or more equivalents of citrate were added, a slight precipitate formed after allowing the solution to stand for a long time. The separation of cadmium(II) and iron (III) ions took place up to the addition of 0.8 equiv. of the complexing agent. With ratios of 1:0.9 to 1:2.9, there was no separation of the ions. With a ratio of 1:3 and above, cadmium (II) ions did not move and only iron (III) ions moved upwards.

FIG. 3

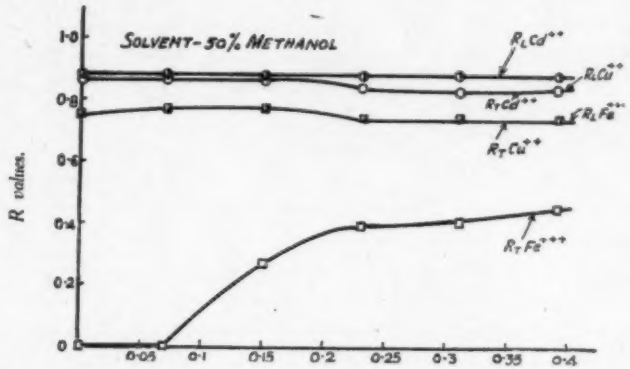
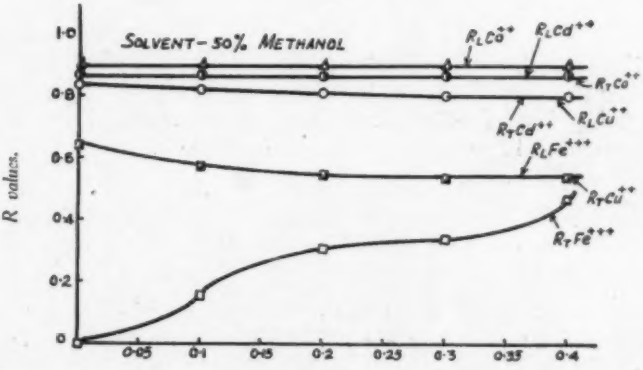


FIG. 4



Separation of Copper (II), *Cobalt* (II), *and Iron* (III).—The separation of cobalt(II), copper(II), and iron (III) (Fig.1) was possible up to the addition of 0.76 equiv. of the complexing agent; with higher concentrations of the same, no separation was possible under the experimental conditions. The R_L values of cobalt(II) and iron(III) did not change with small additions of the complexing agent, but on increasing the concentrations of the same, these increased and became constant. The R_L values of cobalt(II) became constant with 0.53 equiv. of the complexing agent added. The R_L values in case of iron(III) became constant with 0.6 equiv. The R_L value of iron(III) became constant with the addition of 0.47 equiv. of citrate.

Separation of Cobalt (II), *Cadmium* (II), *and Copper*(II).—Separation of the ions in this case (Fig. 2) was possible up to the addition of 0.39 equiv. of citrate. With higher concentrations of the

same, no separation took place; when one or more equivalents of citrate were added only the separation of cadmium (II) ions was possible from cobalt (II) and copper (II) ions. The R_L values of cobalt (II) and cadmium (II) did not change with small additions of citrate and decreased on increasing the concentrations of the same. The R_L values of copper (II) did not change with small additions of citrate, but increased on increasing the concentrations of the same, and finally showed a tendency to become constant.

Separation of Cobalt (II), *Cadmium* (II), *and Iron* (III).—Separation of the ions was effected up to 0.313 equiv. of citrate added; with higher concentration of the same, no separation took place. The R values of cobalt (II) did not change with the addition of citrate. The R_L values of cadmium (II) behaved in a similar manner as in the case of cobalt (II). The R values of iron (III) did not change with small additions of citrate. On increasing the concentrations of the same they tended to increase.

Separation of Cadmium (II), *Copper* (II), *and Iron* (III).—Separation of the ions (Fig. 3) was effected up to the addition of 0.39 equiv. of citrate; with higher concentrations of the same, the separation did not occur due to the spreading and overlapping of the zones. The R values of cadmium (II), copper (II), and iron (III) behaved in a similar manner as described earlier.

Separation of Copper (II), *Cobalt* (II), *Iron* (III), *and Cadmium* (II).—The separation of these ions (Fig. 4) was possible up to 0.4 equiv. of citrate added, but with higher concentration of the same, no satisfactory separation took place due to the spreading of the zones. The R_L values of cobalt (II) and cadmium (II) did not change with additions of citrate. The R_L values of copper (II) and iron (III) decreased with small additions of citrate, then continued to decrease as the concentrations of the same were increased, and finally attained constancy with 0.3 equivalents of citrate added.

Separation of Nickel (II), *Cobalt* (II), *and Copper* (II).—Only the separation of copper (II) ions was effected up to 0.313 equivalents of the complexing agent added.

Separation of Nickel (II), *Cobalt* (II), *and Iron* (III).—The separation of only iron (III) ions was effected from nickel (II) and cobalt (II) ions up to 0.7 equivalent of citrate added. With higher concentrations of the same, no separation took place.

Separation of Nickel (II), *Cadmium* (II), *and Iron* (III).—The separation of iron (III) ions only was possible from the mixture of the ions up to the addition of 0.313 equiv. of citrate; with higher concentration, separation did not occur.

Separation of Copper (II), *Cobalt* (II), *Iron* (III), *and Nickel* (II).—The separation of copper (II) and iron (III) ions only was effected up to 0.4 equiv. of citrate added; but on increasing the concentrations of the same, there was no separation.

Separation of Cobalt (II), *Cadmium* (II), *Nickel* (II), *and Iron* (III).—In the separation of these ions only iron (III) could be separated up to the addition of 0.2 equiv. of the complexing agent.

Separation of Nickel (II), *Cobalt* (II), *Cadmium* (II), *Copper* (II), *and Iron* (III).—Only the separation of copper (II) and iron (III) was effected up to 0.24 equiv. of citrate added. With higher concentrations of the same, no separation took place.

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RHEOCHOR OF BINARY MIXTURES

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It has been observed that the mixture law is applicable to rheochor in case of non-associated binary mixtures.

In several papers from this laboratory (this *Journal*, 1944, **21,** 29; 1948, **25,** 163, 575, 691; 1949, **26,** 533; 1950, **27,** 283, 345; 1951, **28,** 275; 1952, **29,** 303, 691, 706), we have tried to apply the mixture law in case of rheochor. The work has been extended in this paper. The expression employed is

$$R_m = \frac{M_m \gamma^{\frac{1}{4}}}{D}$$

where $R_m = (1-x)R + xR_x$ and $M_m = (1-x)\,M + xM_x$; R_m, M_m, R_x, γ, and D are the rheochor of the solution, mean M.W of the solution, rheochor of the solute, viscosity of the solution, and density of the solution respectively. Our results are summarised in Tables I—IV.

Table I

Rheochor of benzene in toluene.

	Temp. = 30°.			Temp. = 40°.			Temp. = 50°.		
x.	D.	$\gamma\times10^3$.	R_x.	D.	$\gamma\times10^3$.	R_x.	D.	$\gamma\times10^3$.	R_x.
0.0000	0.8467	5.238	..	0.8353	4.700	..	0.8239	4.213	..
0.1316	0.8473	5.318	112.7	0.8399	4.740	110.2	0.8292	4.241	110.2
0.2504	0.8507	5.326	110.4	0.8443	4.775	108.1	0.8334	4.187	111.0
0.3857	0.8541	5.353	110.6	0.8493	4.795	110.6	0.8374	4.292	110.1
0.5971	0.8583	5.426	110.2	0.8516	4.823	111.2	0.8399	4.315	109.8
0.8778	0.8610	5.537	109.9	0.8528	4.837	110.3	0.8429	4.330	111.1
1.0000	0.8640	5.638	..	0.8551	4.892	..	0.8450	4.341	..

$R_{obs} = 110.0$. $R_{calc} = 109.8$.

Table II

Rheochor of methylethyl ketone in toluene.

	Temp. = 30°.			Temp. = 40°.			Temp. = 50°.		
x.	D.	$\gamma\times10^3$.	R_x.	D.	$\gamma\times10^3$.	R_x.	D.	$\gamma\times10^3$.	R_x.
0.0000	0.8467	5.238	..	0.8352	4.700	..	0.8239	4.213	..
0.1630	0.8427	5.173	108.2	0.8318	4.673	107.9	0.8192	4.160	108.0
0.2714	0.8350	5.028	108.4	0.8246	4.536	108.4	0.8136	4.020	108.2
0.4439	0.8295	4.888	108.0	0.8185	4.436	108.2	0.8086	3.895	108.0
0.5380	0.8230	4.738	108.4	0.8123	4.326	108.6	0.8015	3.865	108.3
0.7025	0.8150	4.608	108.5	0.8104	4.310	108.4	0.7826	3.605	108.4
0.8145	0.8122	4.463	109.0	0.8093	4.298	108.9	0.7800	3.465	109.0
1.0000	0.7980	4.365	..	0.7842	4.050	..	0.7706	3.273	..

$R_{obs} = 108.4$. $R_{calc} = 108.4$.

TABLE III

Rheochor of benzene in CCl_4.

	Temp. = 30°.			Temp. = 40°.			Temp. = 50°.		
x.	D.	$\gamma\times10^3$.	R_x.	D.	$\gamma\times10^3$.	R_x.	D.	$\gamma\times10^3$.	R_x.
0.0000	1.6300	8.390	..	1.6160	7.400	..	1.5860	6.580	..
0.1523	1.5200	7.586	109.8	1.4920	6.546	109.8	1.4630	5.598	109.7
0.2945	1.3930	6.252	109.6	1.3650	5.200	109.4	1.3400	4.750	109.6
0.4114	1.2950	5.571	109.6	1.2850	5.115	109.6	1.2560	4.414	109.6
0.5824	1.1800	5.373	109.2	1.1600	4.708	109.4	1.1450	3.988	109.6
0.7230	1.0780	5.208	109.2	1.0600	4.536	109.5	1.0580	3.810	109.5
0.8608	0.9557	5.000	109.3	0.9572	4.312	109.3	0.9408	3.750	109.2
1.0000	0.8638	4.804	..	0.8541	4.244	..	0.8448	3.662	..

$R_{obs}=109.4$ $R_{calc}=109.8$.

TABLE IV

Rheochor of methylethyl ketone in CCl_4.

	Temp. = 30°.			Temp. = 40°.			Temp. = 50°.		
x.	D.	$\gamma\times10^3$.	R_x.	D.	$\gamma\times10^3$.	R_x.	D.	$\gamma\times10^3$.	R_x.
0.0000	1.6300	8.390	..	1.6160	7.400	..	1.5860	6.580	..
0.1725	1.4980	7.563	108.2	1.4720	6.502	108.2	1.4400	5.582	108.3
0.3108	1.3670	6.232	108.4	1.3370	5.187	108.2	1.3240	4.625	108.2
0.4393	1.2510	5.460	108.6	1.2410	5.000	108.2	1.2160	4.375	108.4
0.5820	1.1370	5.000	108.p	1.1340	4.896	108.4	1.1320	4.175	108.6
0.7219	1.0290	4.826	108.0	1.0240	4.658	108.2	1.0002	3.892	108.0
0.8642	0.9237	4.578	108.2	0.9065	4.316	108.2	0.8853	3.596	108.2
1.0000	0.7980	4.365	..	0.7842	4.050	..	0.7706	3.273	..

$R_{obs}=108.2$. $R_{calc.}=108.4$

It will be seen therefore that the mixture law is applicable in case of non-associated liquids studied in this paper.

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N-ACETYL-*N*-PHENYLHYDROXYLAMINE AS A SPECTROPHOTOMETRIC REAGENT FOR IRON

BY H. K. L. GUPTA AND N. C. SOGANI

N-Acetyl-*N*-phenylhydroxylamine furnishes purple, orange, and yellow coloured, water-soluble complexes with Fe(III) at *p*H below 1.2, between 1.8 and 3.5, and above 4.0 with absorbance peaks at 490, 470, and 425 mμ respectively. Pruple-coloured complex is unstable. Orange complex is considered most suitable for detailed study as in its *p*H range there is less interference from foreign ions. The system obeys Beer's law in the concentration range of 1 to 12 p.p.m. of iron at 470 mμ. Most of the commonly associated ions do not interfere. The reaction is not masked by tartrate, phosphate, and cyanide. The sensitivity of the colour reaction, determined in Nessler's cylinder, is 1 part of iron in 4,500,000 parts of solution and on spot plate is 0.2γ of iron. The molecular extinction coefficient at 470 mμ and at *p*H 2.8 is 3.07×10^3.

Shome (*Analyst*, 1950, **75,** 27) has reported the use of *N*-benzoyl-*N*-phenylhydroxylamine as a gravimetric regent for Fe(III), Al(III), and Ti(IV). Earlier (*Curr. Sci.*, 1944, **13**, 257) he reported a list of compounds belonging to 'Cupferron' in which the nitroso group was replaced by R, where R = -CHO, -CO.Me, -CO.Ph, $-CO.NH_2$, -CO.NHPh, $-CS.NH_2$, -CS.NHPh, $-CS.NH.CH_2CH{:}CH_2$. Feigl ("Chemistry of Specific, Selective, Sensitive Reactions", 1949, p. 166, Academic Press Inc., N.Y.) has also indicated the possibility of interesting results from these compounds Preliminary investigation showed that *N*-acetyl-*N*-phenylhydroxylamine exhibited interesting colour reactions with Fe(III). Below *p*H 1.2 it shows purple colour, in *p*H range of 1.8 to 3.5 orange colour, and above *p*H 4.0, yellow colour. Purple-coloured complex is unstable. At higher *p*H there is a possibility of hydrolysis of diverse metal ions. Hence *p*H range between 1.8 and 3.5 is considered to be the most suitable for the spectrophotometric determination of iron either as such or in presence of almost all the commonly associated diverse ions. The development of colour is instantaneous and is stable for a reasonable period (2 hours at 34°). The reaction is not masked by tartrate, phosphate, and cyanide, but is masked by fluoride and oxalate.

EXPERIMENTAL

The Reagent.—Bamberger and Destraz (*Ber.*, 1902, **35,** 1883) have reported the preparation of *N*-acetyl-*N*-phenylhydroxylamine by the action of acetic anhydride on phenylhydroxylamine. We have prepared it by the interaction of acetyl chloride and phenylhydroxylamine in benzene medium according to :

$$\begin{matrix} Ph.N{-}OH \\ | \\ H \end{matrix} + Cl.CO.Me = \begin{matrix} Ph.N{-}OH \\ | \\ CO.Me \end{matrix} + HCl$$

The reaction was carried out in presence of a little water and small lots of sodium bicarbonate were occasionally added to keep the medium slightly alkaline.

Phenylhydroxylamine (10.9 g.) was taken in a 250 c.c. r.b. flask and dissolved in 50 c.c. of benzene. Water (5 c.c.) and sodium bicarbonate (1 g.) were added to it. Acetyl chloride solution (8 g., dissolved in 10 c.c. of benzene) was gradually added from a burette. After each addition the mixture was vigorously shaken till effervescence had ceased. Water layer was kept alkaline to litmus by occasional addition of sodium bicarbonate. In all about 10 g. was required. Near the completion of the reaction, addition of acetyl chloride changed the colour of the reaction mixture from yellow to pink, which on further shaking changed to yellow. At this stage, before adding more acetyl chloride, a drop of reaction mixture was tested with Tollen's reagent. Negative test indicated completion of reaction. It took about $2\frac{1}{2}$ hours for this operation. Benzene layer

was separated. The solvent was evaporated on a water bath. The product solidified on cooling. It was crystallised from hot water and also from benzene-petroleum ether mixture. In both the cases white shining needles were obtained, yield about 10 g., m.p. 66.5° (lit. m.p. 67-67.5°). (Found : N,8.90. Calc. for $C_8H_9O_2N$: N,9.27%).

N-Acetyl-*N*-phenylhydroxylamine is soluble in alcohol, benzene, ether, hot water, and NaOH solution, and it is very slightly soluble in petroleum ether. Its solubility in water at 33.5° is 4.7 g./100g. water. The compound is very stable in solid state, but its solution decomposes, if not stoppered properly.

Standard Fe(III) *Solution.*—AR-ferrous ammonium sulphate (3.92 g.) was oxidised in ammoniacal medium with H_2O_2 and was then dissolved in HCl (dil.) (Clowes and Coleman, "Quantitative Chemical Analysis", 1947, p. 187). It was diluted to give 14 γ of Fe(III) per c.c.

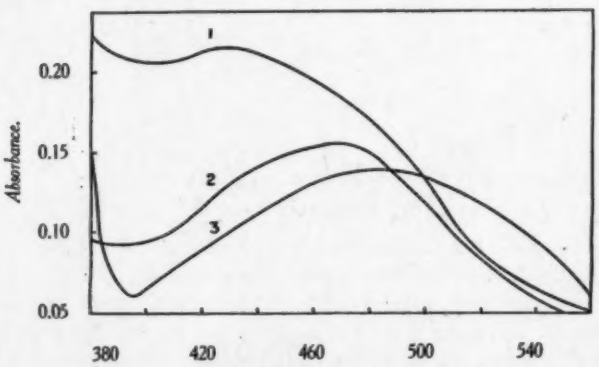
10% HCl (v/v) and 5% sodium potassium tartrate (w/v) were used for adjusting the *p*H. 1.0% Reagent (w/v) solution in distilled water was used.

A Bausch amd Lomb 'Spectronic-20' was used for measuring the absorption, using 1 cm cuvettes. *p*H measurements were made with a Beckman *p*H meter (model H-2). Visual colour comparisons were made with 50 c.c. Nessler's cylinders.

Spectral Characteristics of Iron Complexes.—Each of standard Fe(III) solutions (5 c.c.) containing 14 p.p.m. iron was taken in three 25 c.c. volumetric flasks and 1 c.c. of 5% sodium potassium tartrate solution was added in each flask. Varying amounts of 10% HCl and 1% NaOH solutions were added so that *p*H's of the final solutions were 1.0, 2.6, and 7.0. It was followed by 5 c.c. of the reagent solution and then the volume was made up to the mark. As reagent solution had no absorbance in the visible range, water was used as blank solution.

Fig. 1 shows the spectral characteristics of iron complexes at *p*H values 1.0,2.6, and 7.0. At *p*H 1.0 the colour of the complex is purple with an absorbance peak at 490 mμ (curve 3); at *p*H 2.6, it is orange with an absorbance peak at 470 mμ (curve 2); and at *p*H 7.0 it is yellow with an absorbance peak at 425 mμ (curve 1). Thus formation of different complexes at different H^+ion concentrations is clearly indicated (Harvey and Manning, *J. Amer. Chem. Soc.*, 1950, **72,** 4488).

FIG. 1

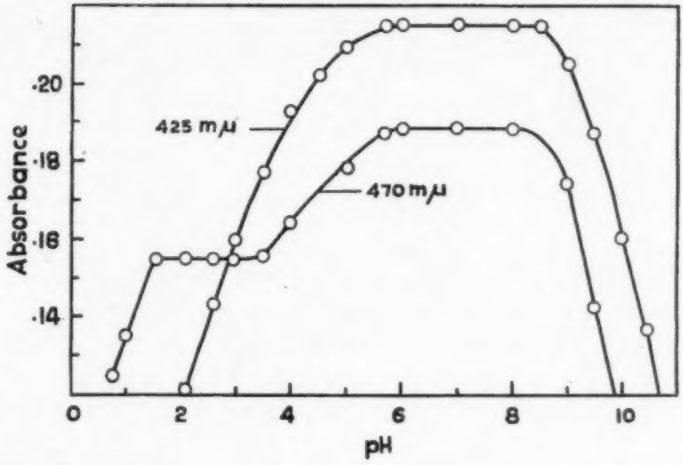


Curve 1, *p*H — 7.0
Curve 2, *p*H — 2.6
Curve 3, *p*H — 1.0

Effect of pH.—Several solutions were prepared, as described above, so that final pH of the solutions ranged between 0.5 and 11.0. Absorbance was measured both at 470 and 425 mμ. At 470 mμ the constant absorbance is in the pH range 1.8 to 3.5 and again between pH 6.0 and 8.5; whereas at 425 mμ the constant maximum absorbance is in the pH range 6.0 to 8.5 (Fig. 2). In all subsequent work use of lower pH range and 470 mμ wave length was preferred as this condition increased the selectivity of the reagent and decreased the possibilities of hydrolysis of diverse ions.

FIG. 2

Effect of pH.

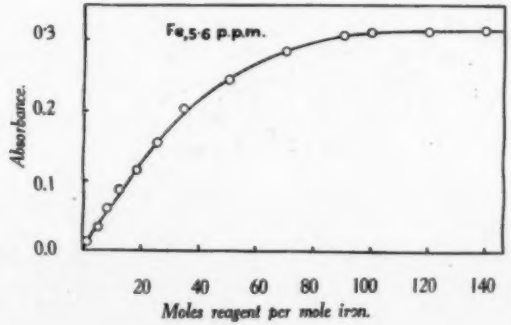


Effect of Time and Stability of Complex.—The full colour development of iron complex is almost instantaneous and is stable over 2 hours at 34°. The fading of the colour has been found to be due to the reducing effect of the reagent on ferric iron.

Effect of Temperature.—The colour of iron complex slightly decreases with an increase in temperature. There is no appreciable difference in absorbance taken at 25° and 35°. Hence maintaining the temperature within 30° ± 5° is considered desirable.

Reagent Concentration and Mole Ratio.—Solutions containing the same amount of iron and different quantities of the reagent were at pH 2.8 and absorbance was measured at 470 mμ. Fig. 3

FIG. 3



shows the effect of increase of moles of the reagent per mole of iron on absorbance. There is a very gradual rise in absorbance, indicating that the iron complex is highly dissociated in dilite solution. Full development of colour is ensured at 1 to 100 ratio of iron to reagent.

Beer's Law.—Beer's law is obeyed in the concentration range of 1 to 12 p.p.m. of iron between *p*H 1.8 and 3.5 and at 470 mμ. The molecular extinction coefficient has been found to be 3.071×10^3.

Sensitivity of Reaction.—Sensitivity of the reaction was determined in Nessler's cylinders in the usual way and was found to be 1 of iron in 4,500.000 parts of solution. Spot plate sensitivity was found to be 0.2 γ of iron in 0.15 c.c. of the solution.

Procedure.—Ferric solution containing 25 to 300 γ of iron was taken into a 25 c.c. volumetric flask; 1 c.c. of 5% sodium potassium tartrate solution and a suitable quantity of 10% HCl were added to it so that *p*H of the final solution was between 1.8 and 3.5. 1% Reagent solution (10 c.c.) was added and the volume made up to the mark. Absorbance was measured at 470 mμ using water as blank.

Tolerance of Diverse Ions.—For studying the interference due to various diverse ions in the determination of iron, the procedure given above was followed. Ag^+, Hg^{2+}, Sn^{4+}, Pb^{2+}, Ce^{4+}, ZrO_2^{2+}, UO_2^{2+}, alkali, and alkaline earth metals do not give any colour reaction and are not likely to interfere. Table I records the results. Only in cases of Cr^{3+}, Co^{2+}, Cu^{2+}, Pd^{2+}, and Pt^{4+} limiting concentrations have been determined. Au(III) is reduced by the reagent; V(IV) gives bluish violet colour and they interfere.

TABLE I

$Fe^{3+} = 2.8$ p.p.m.

Ion.	Added as.	Conc. of ion. (p.p.m.)	Ion.	Added as.	Conc. of ion. (p.p.m.)
Co^{2+}	Sulphate	120	Cr^{3+}	Sulphate	20
Ni^{2+}	,,	320	Bi^{3+}	Nitrate	40
Cu^{2+}	,,	200	Sb^{3+}	Sulphate	40
Mn^{2+}	Chloride	200	Ti^{4+}	,,	50
Zn^{2+}	Sulphate	200	Pt^{4+}	Chloride	12
Cd^{2+}	,,	200	PO_4^{3-}	Sodium	3000
Pd^{2+}	Chloride	20	WO_4^{3-}	,,	40
Al^{3+}	,,	160	CN^-	Potassium	400

Numerous new reagents continue to be proposed for the spectrophotometric determination of iron. The authors (this *Journal*, 1960, **37**, 97) have given a survey of the important reagents proposed for this purpose. *N*-Acetyl-*N*-phenylhydroxylamine is also one of the good reagents. No claim for its superiority over other reagents is made.

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STUDIES IN THIAZOLES. PART IV. PREPARATION OF SOME 2-BROMOTHIAZOLES

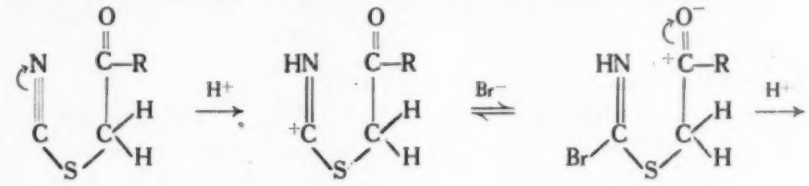
BY N. K. RALHAN, GURMIT SARJIT SANDHU, H. S. SACHDEV AND K. S. NARANG

2-Bromo-4-substituted thiazoles have been synthesised by the treatment of ω-thiocyanoacetophenones with hydrobromic acid gas in dry ether.

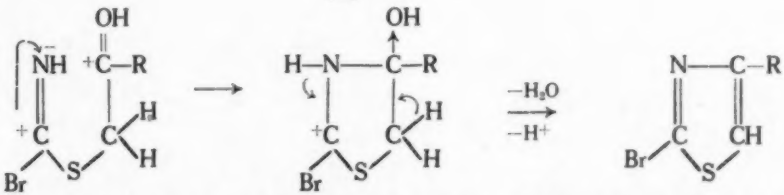
The method available in literature for the preparation of 2-bromothiazoles consists in diazotising 2-aminothiazoles in presence of 30% aqueous hydrobromic acid (Wibaut and Jensen, *Rec. trav. chim.*, 1934, **53**, 77) and the yields by this method are not satisfactory. In a previous attempt (Bariana, Sachdev and Narang, this *Journal*, 1955, **32**, 428) to prepare 2-bromothiazoles by saturating with hydrobromic acid gas an ethereal solution of ω-thiocyanoacetophenone, 2-hydroxy-4-phenylthiazole was found to be the only product in place of the required 2-bromo-4-phenylthiazole.

The sustained efforts in the field reveal that it is absolutely necessary to employ a solvent, which should be free from moisture, and the temperature of the reaction should be below 0°.

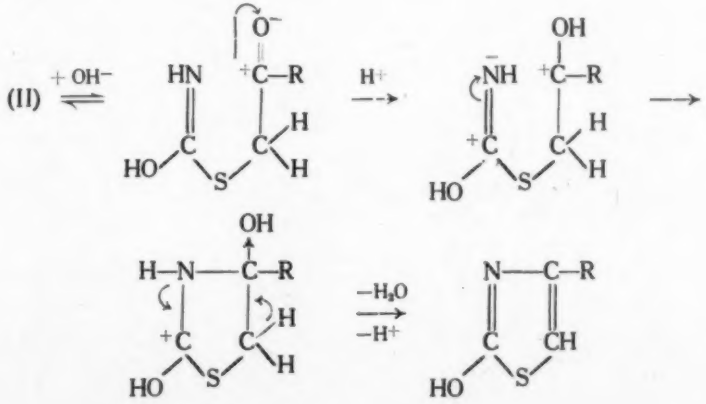
The possible mechanism leading to the formation of 2-bromothiazoles is as follows :



(II)



The traces of moisture possibly facilitate the addition of OH^- in place of Br^- in the intermediate (II), and thus give rise to 2-hydroxythiazoles by proceeding through the following sequence :



2-Bromothiazoles are fairly stable towards aqueous treatments of acidic or neutral solutions and have little tendency to hydrolyse with cold aqueous alkalies. Further work on the synthesis of 2-bromothiazole with various substitutions in the thiazole moiety is in progress.

EXPERIMENTAL

2-Bromo-4-phenylthiazole.—ω-Thiocyano-acetophenone (10 g.), dissolved in dry ether (250c.c.), was cooled in a freezing mixture. It was saturated with dry hydrobromic acid for about 2 hours and allowed to stand for further 3 hours. The solvent was removed by distillation and the solid so obtained was treated with sodium carbonate solution, and filtered. On crystallisation from dilute ethanol it furnished a white solid, m.p. 55°, yield 8.0 g. (Found : S, 13.60. C_9H_6NBrS requires S, 13.33%).

TABLE I

2-Bromo-4-substituted thiazoles.

Compound.	Formula.	M.P.	Yield.	Found.	Calc.
2-Bromo-4-(*p*-chlorophenyl)-T	$C_9H_5NBrClS$	110°	70.8%	N: 5.23	5.24
2-Bromo-4-(*p*-ethoxyphenyl)-T	$C_{11}H_{10}ONBrS$	105°	60.8	N: 4.72	4.93
2-Bromo-4-(*p*-bromophenyl)-T	$C_9H_5NBr_2S$	120°	86.6	Br: 50.70	50.15
2-Bromo-4-(*p*-methoxyphenyl)-T	$C_{10}H_8ONBrS$	135°	50.6	N: 5.57	5.18
2-Bromo-4-(*p*-ethylphenyl)-T	$C_{11}H_{10}NBrS$	60-61°	61.0	N: 5.06	5.22
2-Bromo-4-(*p*-methylphenyl)-T	$C_{10}H_8NBrS$	89-90°	80.0	C: 47.96 H: 3.35	47.24 3.15
2-Bromo-4-(4'-methyl-6'-hydroxy-phenyl)-T	$C_{10}H_8ONBrS$	165°	60.1	N, 5.35	N, 5.18

Note : Ethanol was used as the solvent for the crystallisation of the compounds.
T denotes thiazole.

A similar experimental procedure was adopted for the preparation of some other 2-bromo-4-substituted thiazoles (Table I). In some cases α-thiocyano-ketone did not dissolve in the requisite amount of ether, which, however, dissolveed as the reaction proceeded in the forward direction.

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IODINATION OF SOME COUMARIN DERIVATIVES*

By S. S. Lele, M. G. Patel and Suresh Sethna

The iodination of 7-hydroxycoumarin and substituted 5- and 7-hydroxycoumarins, and their methyl ethers with substituents, such as, carboxyl, carbomethoxyl and nitro groups, has been studied using different iodinating agents.

The work on the iodination of coumarin derivatives has been extended; the iodination of several 7- and 5-hydroxycoumarin derivatives has been studied, using (*a*) iodine monochloride, (*b*) iodine and iodic acid ($5RH + 4I + HIO_3 \longrightarrow 5RI + 3H_2O$), and (*c*) iodine and ammonia as iodinating agents.

7-Hydroxycoumarin on iodination, by the three methods, with theoretical amounts of the iodinating agents furnished in each case the 8-iodo derivative. Its methyl ether neither gave a coumarilic acid derivative on boiling with alkali nor did it undergo the Elbs persulphate oxidation, indicating that the iodine had not entered either the 3- or the 6-position (cf. Dalvi, Desai and Sethna. this *Journal*, 1953, **30**, 610). With two moles of iodine in presence of ammonia the 6:8-diiodo compound was obtained. Its methyl ether remained unchanged on boiling with alkali. The 3: 6: 8-triiodo derivative was obtained on iodination with double the theoretical amounts of iodine and iodic acid, and with excess of the other two iodinating agents. Its methyl ether furnished a diiodocoumarilic acid derivative on boiling with alkali.

7-Methoxycoumarin gave with one mole of iodine monochloride the 3-iodo derivative. With alkali it afforded the known 6-methoxycoumarilic acid (Seshadri and Varadrajan, *J. Sci. Ind. Res.*, 1952, **11B**, 39). The other two methods did not yield any iodo product. With four moles of iodine monochloride it gave the 3: 6-diiodo derivative. Its methyl ether furnished a monoiodocoumarilic acid. Further, it was different from the 3: 8-diiodo derivative, synthesised by iodinating the 7-methoxy-8-iodocoumarin with iodine monochloride, and which gave an isomeric monoiodocoumarilic acid.

The iodination of 7-hydroxycoumarin-6-carboxylic acid, 7-hydroxy-4-methylcoumarin-6-carboxylic acid, and its methyl ester and methyl 5-hydroxy-4-methylcoumarin-6-carboxylate with theoretical amounts of the iodinating agents gave the corresponding 8-iodo derivatives by the three methods. The methyl ethers of the iodo-coumarin esters on hydrolysis afforded only the corresponding coumarin carboxylic acids. In no case was a coumarilic acid derivative formed. No further iodination of the above coumarins could be achieved by any of the three methods except in the case of 7-hydroxycoumarin-6-carboxylic acid, which on iodination with double the quantities of iodine and iodic acid gave the 3: 8-diiodo derivative, the methoxy derivative of which furnished a monoiodocoumarilic acid.

* Previous paper: S. S. Lele and Suresh Sethna, *J. Org. Chem.*, 1958, **23**, 1731.

On iodination with one mole of iodine monochloride, methyl 7-methoxycoumarin-6-carboxylate and its 4-methyl analogue gave the 3-iodo derivatives, which were degraded to the corresponding coumarilic acid derivatives with alkali. The methoxy esters could not be iodinated by the other two methods. Methyl-5-methoxycoumarin-6-carboxylate and its 4-methyl analogue gave monoiodo derivatives, which could not be degraded to the corresponding coumarilic acid derivatives and were therefore assigned the 8-iodo structures. For the same reason the product obtained on the iodination of 7-hydroxy-6-nitro-4-methylcoumarin with iodine and iodic acid was assigned the 8-iodo structure. This nitrocoumarin could not be iodinated by the other two methods, and further iodination with iodine and iodic acid could not be achieved.

In the iodination of 7-hydroxy-4-methylcoumarin-8-carboxylic acid with iodine and ammonia, the carboxyl group was eliminated and the known 7-hydroxy-8-iodo-4-methylcoumarin was obtained.

7-Hydroxycoumarin-4-acetic acid yielded the 8-iodo derivative on iodination by all the three methods. Methyl ether of the ester of this iodocoumarin on alkaline hydrolysis lost the carbomethoxy group and gave the known 7-methoxy-8-iodo-4-methylcoumarin. On iodination with two moles of iodine in presence of ammonia, the 6 : 8-diiodo derivative was obtained. During methylation of this compound decarboxylation occurred, and the known 7-methoxy-6 : 8-diiodo-4-methylcoumarin was obtained. No triiodo derivative was obtained with excess of iodine and ammonia, but with double the quantities of iodine and iodic acid, the 3 : 6 : 8-triiodo derivative was obtained. During methylation it underwent decarboxylation and provided the known 7-methoxy-3 : 6 : 8-triiodo-4-methylcoumarin.

EXPERIMENTAL

General Iodination Procedures

(*a*) *With Iodine Monochloride.*—To the coumarin derivative (0.01*M*), dissolved in minimum quantity of glacial acetic acid, HCl (*d* 1.1, 15 c.c.) was added. The mixture was added to the requisite amount of iodine monochloride and kept for 24 hours at 50°. The iodo derivative, which separated from the solution as such or on dilution with water, was crystallised from acetic acid. In the case of methoxycoumarin derivatives the iodination products were not readily obtained if hydrochloric acid was used, and hence it was dispensed with.

(*b*) *With Iodine and Iodic Acid.*—The coumarin derivative (0.01 *M*) was dissolved in minimum quantity of warm ethanol and the requisite amount of iodine was added. To the warm dark coloured solution obtained the required amount of iodic acid, dissolved in water, was added with stirring. The reaction mixture was stirred for 2 hours and the iodo derivative, which separated as such or on dilution with water, was crystallised from acetic acid.

(*c*) *With Iodine and Ammonia.*—To the coumarin derivative (0.01*M*), dissolved in dilute ammonia, a solution of iodine in potassium iodide in required quantity was added with stirring at room temperature during 1/2 hour. The reaction mixture was then poured into excess of dilute ice-cold sulphuric acid. The precipitated iodo derivative was crystallised from acetic acid.

Products obtained on iodination by the three methods are recorded in Table I.

Preparation of Methyl Ethers.—The iodo derivatives were methylated by refluxing their acetone solutions with dimethyl sulphate in presence of anhydrous potassium carbonate (Table II).

Hydrolysis of Methoxyiodocoumarins.—The methoxyiodocoumarins were hydrolysed by boiling with 10% ethanolic KOH for 2 hours (Table III).

TABLE I

Products obtained on iodination.

No.	Coumarin.	Method.	Product.	*M.P.	% Yield.	Formula.	% Iodine Found.	% Iodine Calc.
1.	7-Hydroxy-	a,b,c,	8-Iodo	228-32°	10,49,80	$C_9H_5O_3I$	44.1	44.1
		c	6:8-Diiodo	232°	9	$C_9H_4O_3I_2$	61.7	61.3
		a,b,c.	3:6:8-Triiodo	235°	56	$C_9H_3O_3I_3$	70.5	70.6
2.	7-Methoxy-	a	3-Iodo	155-56°	17	$C_{10}H_7O_3I$	42.3	42.4
		a	3:6-Diiodo	246-47°	47	$C_{10}H_6O_3I_2$	59.4	59.3
3.	7-Methoxy-8-iodo-	a	3:8-Diiodo	238°	46	$C_{10}H_6O_3I_2$	59.5	59.3
4.	7-Hydroxy-6-carboxy-	a,b,c.	8-Iodo	258-60°	45,54,9	$C_{10}H_5O_6I$	38.4	38.3
		b	3:8-Diiodo	272°	11	$C_{10}H_4O_6I_2 \cdot 2H_2O$†	50.8	51.4
5.	7-Methoxy-6-carbomethoxy-	a	3-Iodo	245-46°	72	$C_{12}H_9O_6I$	35.2	35.3
6.	7-Hydroxy-4-acetic acid	a,b,c.	8-Iodo	227-28°	72,58,72	$C_{11}H_7O_6I$	36.6	36.7
		c	6:8-Diiodo	235-36°	74	$C_{11}H_6O_6I_2 \cdot H_2O$**	51.8	51.8
		b	3:6:8-Triiodo	238-40°	67	$C_{11}H_5O_6I_3$	64.2	63.7
7.	5-Methoxy-6-carbomethoxy	a	8-Iodo	157-58°	31	$C_{12}H_9O_6I$	34.7	35.3
8.	7-Hydroxy-4-methyl-6-carboxy-	c	8-Iodo	273°	66	$C_{11}H_7O_6I$	36.7	36.7
9.	7-Hydroxy-4-methyl-6-carbomethoxy-	a,b,c.	8-Iodo	285°	13,53,76	$C_{12}H_9O_5I$	35.0	35.3
10.	7-Methoxy-4-methyl-6-carbomethoxy-	a	3-Iodo	234°	66	$C_{13}H_{11}O_5I$	34.1	33.9
11.	7-Hydroxy-4-methyl-8-carboxy-	c	7-Hydroxy-8-iodo-4-methylcoumarin	..	..	..	..	..
12.	5-Hydroxy-4-methyl-6-carbomethoxy-	a,b.	8-Iodo	254°	21,48	$C_{12}H_9O_6I$	35.4	35.3
13.	5-Methoxy-4-methyl-6-carbomethoxy-	a	8-Iodo	154°	54	$C_{13}H_{11}O_6I$	34.2	33.9
14.	7-Hydroxy-4-methyl-6-nitro-	b	8-Iodo	273°	62	$C_{10}H_6O_5NI$	36.1	36.6

* All the melting points are uncorrected. Hydroxyiodo derivatives start decomposing 20-30° below their melting points and melt finally at the mentioned temperatures.
† Analysis after drying at 110° in vacuum. Found: I, 53.0%. $C_{10}H_4O_6I_2.H_2O$ requires I, 53.3%.
** The product decomposes on drying at 110° in vacuum.

TABLE II

Methyl ethers of the hydroxyiodocoumarins.*

No.	Coumarin.	M.P.	Formula.	%Carbon. Found.	%Carbon. Calc.	%Hydrogen. Found.	%Hydrogen. Calc.	%Iodine. Found.	%Iodine. Calc.
1	7-Methoxy-8-iodo-	158°	$C_{10}H_7O_3I$	40.1	40.0	2.5	2.3	41.9	42.4
2.	7-Methoxy-6:8-diiodo-	168-70°	$C_{10}H_6O_3I_2$	27.6	28.0	1.5	1.4	59.0	59.3
3.	7-Methoxy-3:6:8-triiodo-	208-10°	$C_{10}H_5O_3I_3$	21.9	21.7	1.2	0.9	68.2	68.8
4.	7-Methoxy-8-iodo-6-carbomethoxy-	162°	$C_{12}H_9O_5I$	39.6	40.0	2.8	2.5	35.6	35.3
5.	7-Methoxy-3:8-diiodo-6-carbomethoxy-	205-206°	$C_{12}H_8O_5I_2$	29.5	29.6	2.1	1.6	52.3	52.3
6.	7-Methoxy-8-iodo-4-carbomethoxymethyl-	140-42°	$C_{13}H_{11}O_5I$	42.2	41.7	3.3	2.9	34.1	33.9
7.	7-Methoxy-8-iodo-4-methyl-6-carbomethoxy-	223°	$C_{13}H_{11}O_5I$	41.6	41.7	2.9	2.9	33.9	33.9
8.	7-Methoxy-8-iodo-4-methyl-6-nitro-	242°	$C_{11}H_8O_5NI$	36.2	36.6	2.1	2.2	34.8	35.2

* Mentioned in Table I.

TABLE III

Hydrolysis products of the methoxyiodocoumarins.

No.	Coumarin.	Product.	M.P.	Formula.	% Carbon. Found.	% Carbon. Calc.	% Hydrogen. Found.	% Hydrogen. Calc.	% Iodine. Found.	% Iodine. Calc.
1.	7-Methoxy-3:6-diiodo-	6-Methoxy-5-iodo-coumarilic acid	258°	$C_{10}H_7O_4I$	37.5	37.7	2.2	2.2	39.8	39.9
2.	7-Methoxy-3:8-diiodo-	6-Methoxy-7-iodo-coumarilic acid	280°	$C_{10}H_7O_4I$	37.5	37.7	2.6	2.2	40.4	39.9
3.	7-Methoxy-3:6:8-triiodo-	6-Methoxy-5:7-diiodocoumarilic acid	240°	$C_{10}H_6O_4I_2$	27.4	27.0	1.8	1.4	57.2	57.2
4.	7-Methoxy-3-iodo-6-carbomethoxy-	6-Methoxy-5-carboxycoumarilic acid	285°	$C_{11}H_8O_6$	56.2	55.9	3.4	3.4	..	..
5.	7-Methoxy-8-iodo-6-carbomethoxy-	7-Methoxy-8-iodo-coumarin-6-carboxylic acid	236°	$C_{11}H_7O_5I$	38.5	38.2	2.3	2.0	36.8	36.7
6.	5-Methoxy-8-iodo-6-carbomethoxy-	5-Methoxy-8-iodo-coumarin-6-carboxylic acid	238°	$C_{11}H_7O_5I$	38.0	38.2	2.4	2.0	37.0	36.7
7.	7-Methoxy-3:8-diiodo-6-carbomethoxy-	6-Methoxy-7-iodo-5-carboxycoumarilic acid	272°	$C_{11}H_7O_6I$	37.0	36.5	2.2	1.9	34.7	35.1
8.	7-Methoxy-8-iodo-4-carbomethoxymethyl-	*7-Methoxy-8-iodo-4-methylcoumarin	..	..	..	..	..	..	..	..
9.	7-Methoxy-3-iodo-4-methyl-6-carbomethoxy-	**6-Methoxy-5-carboxy-3-methylcoumarilic acid	..	..	..	..	..	..	..	..
10.	7-Methoxy-8-iodo-4-methyl-6-carbomethoxy-	7-Methoxy-8-iodo-4-methylcoumarin-6-carboxylic acid	237°	$C_{12}H_9O_5I$	39.8	40.0	2.3	2.5	35.2	35.3
11.	5-Methoxy-8-iodo-4-methyl-6-carbomethoxy-	5-Methoxy-8-iodo-4-methylcoumarin-6-carboxylic acid	245°	$C_{12}H_9O_5I$	39.6	40.0	2.3	2.5	35.6	35.3

* Lele and Sethna (*loc. cit.*).

** Dalvi and Sethna, this *Journal*, 1949, **26**, 359, 467.

6-Hydroxy-7-methoxy-8-iodocoumarin.—7-Methoxy-8-iodocoumarin (3.02 g.) was dissolved in 10% NaOH solution (80 c.c.) by warming on a steam bath. It was then oxidised with potassium persulphate (2.5 g. in 120 c.c. water) according to the procedure described by Parikh and Sethna (this *Journal*, 1950, **27**, 369). The product obtained was crystallised from dilute ethanol in needles, m.p. 217°. (Found: C, 37.7; H, 2.5; I, 39.9. $C_{10}H_7O_4I$ requires C, 37.7; H, 2.2; I, 39.9%).

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THE CHEMISTRY OF FLUOCHLORATES. PART I. FLUOCHLORATES OF COPPER, ZINC, CADMIUM, NICKEL, COBALT, CALCIUM, STRONTIUM, BARIUM, AND LEAD

BY ASIMBIKASH RAY AND GRIHAPATI MITRA

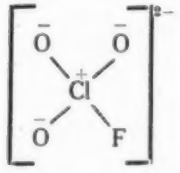
The fluochlorates of Cu, Zn, Cd, Pb, Ba, Ca, Sr, etc. have been described. Copper, zinc, nickel, cadmium, and cobalt fluochlorates are soluble in water. The other fluochlorates are insoluble in water. From the X-ray data the nickel fluochlorate hexahydrate is found to be isomorphous with zinc monofluoroarsenate hexahydrate. Nickel and cobalt fluochlorates crystallise with six or seven molecules of water. Fluochlorates are oxidising agents. The soluble fluocholrates have been found to form mixed crystals with the corresponding sulphates, fluoroberyllates, etc.

The complex anions formed by the halogens are well known. Those formed by chlorine are ClO_2^-, ClO_3^-, and ClO_4^-. It is of interest to note that no oxyfluoro complex ion of chlorine is known. Iodine forms an oxyfluoro anion, $IO_2F_2^-$. The difluorodioxo-iodates have been studied by Rogers and Helmholz (*J. Amer. Chem. Soc.*, 1940, **62**, 1537).

The existence of the fluochlorates and monofluorotrioxyiodates has already been established by Ray and Mitra (*Science & Culture*, 1956, **21**, 379; this *Journal*, 1958, **35**, 211). The fluochlorates of Cu, Zn, Cd, Ni, Co, Ca, Sr, Ba, and Pb have been studied in the present communication.

The structure of the fluochlorates in keeping with the dichlorodioxo-iodates should be as :

(in fluochlorate)



Hence this p^3d or p^3s hybridisation would have resulted in a more or less regular tetrahedron but for the lone pair of electrons in the 3s level. The lone pair hybridisation distorts the structure, and therefore the structure is not comparable to that of the perchlorate ion.

EXPERIMENTAL

Fluochlorates were prepared from C.P. and A.R. quality of reagents. The compounds were decomposed by fusion with alkali carbonates. The amounts of fluorine and chlorine were determined from the extract obtained by leaching the fused mass with hot water. The metals were estimated after converting the respective compounds into their corresponding sulphates by slowly heating them with H_2SO_4 (conc.) (Treadwell and Hall, "Analytical Chemistry", Vol. II).

Copper Fluochlorate Pentahydrate.—To a weighed amount of copper carbonate, taken in a platinum basin, 40% chloric acid was added to decompose the carbonate, last traces of which were removed by heating on a water bath. An equivalent amount of copper carbonate, taken in another platinum basin, was decomposed by addition of 40% HF. Pure CuF_2 not being sufficiently soluble in water, the excess of the acid was removed by decantation. The presence of a slight excess of hydrofluoric acid, however, has no harmful effect on the final product. To the copper fluoride, thus obtained, copper chlorate solution was added, and the mixture digested on a water bath for about 15 minutes, and then HNO_3 (conc.) was added dropwise with constant stirring till a clear solution was obtained. The solution was digested on the water bath for a further period of an hour, cooled to room temperature, and filtered to remove the insoluble impurities. The clear filtrate was kept in a vacuum desiccator over H_2SO_4. After a few days blue crystals appeared, which were filtered under suction, washed once with water, and then with 60% ethanol, and dried in the air. (Found : Cu, 24.80; Cl, 13.78; F, 7.28. $CuClO_3F$, $5H_2O$ requires Cu, 24.83; Cl, 13.85; F, 7.42%). It is highly soluble in water and also in 60% ethanol.

Zinc fluochlorate heptahydrate was prepared in the way described above. It was observed that during the preparation of this compound addition of nitric acid was not necessary; the fluoride itself dissolved in a solution of zinc chlorate. (Found : Zn, 22.02; Cl, 12.00; F, 6.30. $ZnClO_3F$, $7H_2O$ requires Zn, 22.24; Cl, 12.07; F, 6.46%).

This compound is also highly soluble in water. The equivalent conductivity of zinc fluochlorate solutions of different concentrations was determined at 35° (Table I).

TABLE I

Conc.	*M*/32	*M*/64	*M*/128	*M*/256	**M*/1024
Conduc.	50	76	95	108	124

* Conductivity at 25° became 102 (∼).

From the results it appears that in solution there are only two ions :

$$ZnClO_3F \rightleftharpoons Zn^{2+} + ClO_3F^{2-}$$

Some amount of auto-complex formation is also indicated in a concentrated solution.

Cadmium fluochlorate 8/3 hydrate was obtained by the same method as in the case of the copper compound. On account of excessive solubility of cadmium fluochlorate a white slime, instead of crystals, was obtained. (Found : Cd, 42.56; Cl, 13.40; F, 6.96. $CdClO_3F$, 8/3 H_2O requires Cd, 42.76; Cl,13.49; F, 7.23%).

Nickel fluochlorate heptahydrate was obtained by the method described above. (Found : Ni, 20.42; Cl, 12.30 ; F, 6.50. $NiClO_3F$, $7H_2O$ requires Ni, 20.44; Cl, 12.35; F, 6.62%). It is highly soluble in water.

Solutions of the fluochlorates, in general, do not form any precipitate with calcium chloride in the cold and do so very slowly on boiling. The fluorine atom is therefore more strongly attached to the central element in the case of ClO_3F^{2-} ion than in BF_4^-, one of the most stable fluoride complex anions. This is in keeping with the fact that the Cl—F link is more covalent in character than the B-F link. This compound slowly passes into the hexahydrated form at 30°. (Found : Ni, 21.82. $NiClO_3F$, $6H_2O$ requires Ni, 21.80%).

The powder picture of the hexahydrated nickel fluochlorate was taken. The result is shown in Table II.

TABLE II

D (in K_α unit)	*Intensity.	D (in K_α unit)	*Intensity.	D (in K_α unit)	*Intensity.
4.689	V. S.	2.297	W.	1.469	M. W.
4.130	S.	2.167	W.	1.376	M. W.
3.082	M. W.	2.062	M.	1.186	W.
2.894	M.	1.873	M. S.	1.116	W.
2.572	S.	1.599	M. S.	1.091	

* V. S.=very strong. S.=Strong. M. S.=Medium strong. M. W.=Medium weak. W=Weak. V. W.=Very weak.

It is of interest to note that this compound is found to be isomorphous with $ZnAsO_3F$, $6H_2O$ (Mitra, *Science & Culture*, 1953, **19**, 216; Ray and Mitra, unpublished data). It suggests therefore that in AsO_3F^{2-}, due to the inert nature of the 4S electrons, the hybridisation has taken place in the p^3d level. It must be noted, however, that the lone pair hybridisation taking place with arsenic and chlorine atoms in AsO_3F^{2-} and ClO_3F^{2-} respectively has resulted in a similar deformation. Further study is necessary to prove this phenomenon.

Cobalt fluochlorate heptahydrate was obtained by following the general method of preparation of the soluble fluochlorates, described above. (Found : Co, 20.40; Cl, 12.32; F, 6.50. $CoClO_3F$, $7H_2O$ requires Co, 20.50; Cl, 12.33; F, 6.61%).

When a concentrated solution of this compound was heated on a water bath, the hexahydrated salt crystallised out. (Found : Co, 21.80. $CoClO_3F$, $6H_2O$ requires Co, 21.90%).

The fluochlorates, described above, are soluble in water. It has been observed that in solution the secondary dissociation of this ion into free fluoride and chlorate ions is negligible. Addition of calcium chloride solution therefore does not result in the precipitation of calcium fluoride. All these fluochlorates form mixed crystals with the corresponding sulphates, fluoberyllates, oxyfluoborates, etc. The fluochlorates, mentioned above, form double salts with alkali metal sulphates or fluoberyllates; the molecular formulas of these double salts are similar to those of Tutton's salts. The fluochlorates like the chlorates and perchlorate exhibit oxidising properties. When the soluble fluochlorates are treated with solutions of barium chloride, calcium chloride, strontium nitrate, or lead nitrate, the sparingly soluble fluochlorates of these metals are formed. During the time of preparation of the calcium salt, a few drops of ethanol were added in order to suppress the secondary dissociation. The following fluochlorates were isolated.

Calcium fluochlorate was isolated as a very fine white precipitate. (Found : Ca, 27.85; Cl, 24.60. $CaClO_3F$ requires Ca, 28.11; Cl, 24.87%).

Strontium fluochlorate : (Found : Sr, 46.00; Cl, 18.44; F, 9.76. $SrClO_3F$ requires Sr, 46.10; Cl, 18.65; F, 10.00%).

Barium fluochlorate is the least soluble fluochlorate isolated. (Found : Ba, 57.10; Cl, 14.65; F, 7.78. $BaClO_3F$ requires Ba, 57.27; Cl, 14.78; F, 7.92%).

Lead fluochlorate was obtained by treating a concentrated solution of nickel fluochlorate with lead nitrate. (Found : Pb, 66.42; F, 6.00. $PbClO_3F$ requires Pb, 66.91; F, 6.13%).

These sparingly soluble fluochlorates have been found to be slightly more soluble in water that the corresponding sulphates.

The authors are indebted to Dr. N. N. Ray, D.Sc., formerly of the Presidency College, Calcutta, for providing us with all laboratory facilities during the progress of this work.

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CONDUCTOMETRIC STUDY OF THE REACTION BETWEEN ALUMINIUM NITRATE AND ALKALI

BY B. R. GUHA AND B. P. GYANI*

Reactions between aluminium nitrate and alkalies (NaOH, NH_4OH) have been studied conductometrically. Different results have been obtained regarding composition of compounds formed, which appears to depend upon the prevailing *p*H, ionic concentration, and ageing. By suitable choice of conditions pure Na_2HAlO_3, $Al(OH)_3$, and nearly pure $NaAlO_2$ may be formed. Freshly precipitated $Al(OH)_3$ may also be quantitatively converted into $AlCl_3$, during titration with HCl.

The earlier conductometric work on the reactions between aluminium salts and alkalies has been summarised by Britton ("Conductometric Analysis", p. 139, Chapman & Hall, London, 1934). Both Kolthoff (*Z. anorg. allgem. Chem.*, 1920, **112**, 172) and Britton (*loc. cit.*) used aluminium sulphate and NaOH. Kolthoff carried out conductometric titrations both under increasing and decreasing *p*H and found the latter more helpful for precipitation of pure $Al(OH)_3$ provided that the temperature was not low. Britton obtained a number of breaks when the *p*H was increasing (0.003125*M* sulphate, 0.20*M*-NaOH), which they ascribed to basic salts and $NaAlO_2$, but no break agreed with pure $Al(OH)_3$.

The nitrate has to be preferred since NO_3^- is less prone to complex formation or adsorption. The results with NaOH deserve to be compared with those obtained with NH_4OH. Back-titration of salt—alkali mixtures with mineral acids may throw additional light on the reactions. These titrations were therefore undertaken.

EXPERIMENTAL

An accuracy better than 1% was easily assured by using a precision bridge, a valve oscillator, and a cell with inaccessible electrodes. The titrations were performed with alkali in the cell (decreasing *p*H) and the reverse. The results are shown in Table I and the titration graphs bearing the same numbers in Figs. 1-4.

TABLE I

No.	Cell.	Burette.	Inflection. Required for.	Found.	Remarks.
1a	2 c.c. of 0.480*N* Al nitrate + 18c.c. water	0.505*N*-NaOH	i. $Al(OH)_3$ = 1.90 ii. $NaAlO_2$ = 2.53	B. 1.75 C. 2.45	30°. Colloidal ppt. from 0.4c.c.; heavy gelatinous ppt. from 1.9c.c. and dissolving from 2.6 c.c.
1b	Do	Do	Do	i. 1.80 ii. 2.45	28°. Mixture heated to 80° after every addn. of alkali, then cooled.
1c	2c.c. of 0.5155*N* salt + 148c.c. water	0.505*N*-NaOH	i. $Al(OH)_3$ = 2.04 ii. $NaAlO_2$ = 2.72	i. 2.00 ii. 2.55	Bath temp. = 30°.
2a	1c.c. of 1.01*N*-NaOH + 19 c.c. water	0.480*N* salt	i. $NaAlO_2$ = 1.575 ii. $Al(OH)_3$ = 2.10	i. 1.50 ii. 2.20	29°. Ppt. from 1.6, redissolved from 2.3. Extrapolated value for (ii) = 2.1.
2b	Do	Do	Do	i. 1.50 ii. 2.10	28°. Mixture heated as in 1b.
2c	1 c.c. of 1.01*N*-NaOH + 149 c.c. water	0.5155*N* salt	i. $NaAlO_2$ = 1.469 ii. $Al(OH)_3$ = 1.96	i. 1.40 ii. 1.96	Bath temp. = 30°.
3a	10c.c. of 0.048*N* salt + 45 c.c. of 0.093*N*-NaOH	1*N*-HCl	i. NaOH left = 3.73 ii. $AlCl_3$ = 4.18	i. 3.40 ii. 4.20	30°. Ppt. from 3.6 c.c., redissolved from 4.0 c.c. $Al(OH)_3$ stage would consume 0.48 c.c. of *N*-NaOH against 0.785 c.c. consumed at (i).
3b	40c.c. of 0.024*N* salt + 40 c.c. of 0.093*N*-NaOH	Do	i. NaOH left = 2.76 ii. $AlCl_3$ = 3.72	i. 2.25 ii. 3.45	31.5°. $Al(OH)_3$ stage would consume 0.96c.c. *N*-NaOH against found 1.47. Alkali retained at (ii)=0.27 against required nil. Ppt from 2.5c.c.; redissolved from 3.0 c.c. acid.
3c	20 c.c. of 0.048*N* salt + 40 c.c. of 0.093*N*-NaOH	Do	Do	Do	32° Do

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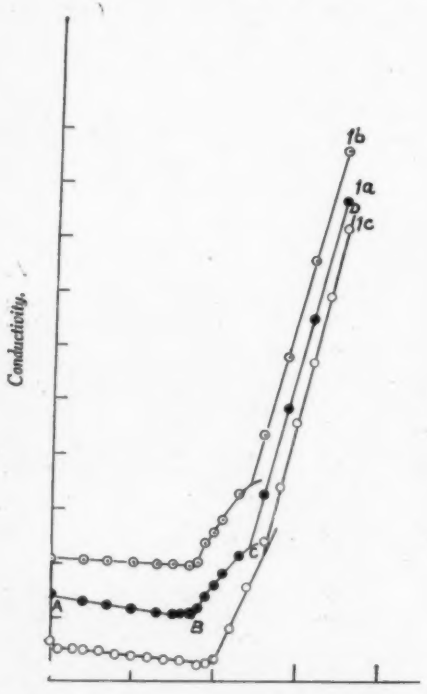
TABLE I (*contd.*)

No.	Cell.	Burette.	Inflection. Required for.	Found.	Remarks.
4a	5c.c. of 0.48*N* salt+2c.c. water	0.978*N*-NH_4OH	$Al(OH)_3 = 2.45$	2.55	30°. Colloidal ppt. from 2.4. Gelatinous ppt. from 2.5.
4b	5c.c. of 0.48 *N* salt+2c.c. of *N*-NH_4Cl+18c.c. water	Do	Do	Do	Do
4c	Salt same + 20c.c. o.1*N*-KCl	Do	Do	Do	Do
5	1c.c. of 0.978 *N* NH_4OH+19c.c. water	0.48*N* salt	$Al(OH)_3 = 2.04$	1.95	31°. Ppt. from 0.5c.c.; redissolved from 2.0c.c.

DISCUSSION

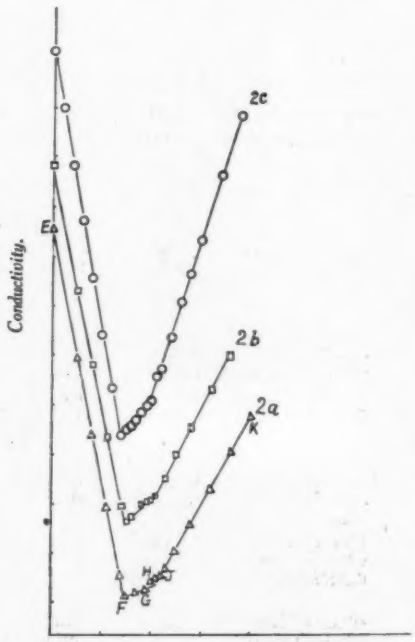
Titration of $Al(NO_3)_3$ *with* NaOH.—In the titration (1a) the first break B occurs at 1.75 c.c of NaOH (2.763 equiv. per mole salt). Since the mobilities of $\frac{1}{3}Al^{3+}$ and Na^+ are practically equal (about 41 at 18°) the slope of AB is small. B corresponds to 12 $Al(OH)_3$,$Al(NO_3)_3$, but it is safer to consider it to be an adsorption compound as there is a fine colloidal precipitate from the commencement.

FIG. 1



Titration of $Al(NO_3)_3$ *with* NaOH.

FIG. 2



Titration of NaOH *with* $Al(NO_3)_3$.

Another break occurred at C=3.87 equiv. (required 4.0 equiv. for $NaAlO_2$). It appears that about 3% of the precipitate formed at first is rendered insoluble due to ageing. This is supported by a turbidity, which persists even at D (excess alkali).

In the titration (1b) the mixture was heated to 80° after every addition of alkali and then cooled to thermostat temperature. The break corresponding to B was then much sharper, perhaps due to reduced adsorption. The second inflection maintained its location.

With more dilute salt solution (1c) the discrepancy in B was reduced to 2%, but that in C was increased to over 6% and the residual turbidity was more pronounced. It appears that reduction in ionic concentration may increase the ageing effect.

Titration of NaOH *with* $Al(NO_3)_3$.—When the titrations were reversed, the usual precipitation of $Al(OH)_3$ appeared momentarily and soon disappeared in the excess alkali. There could be no question of ageing, and we expected the first break at 1.575 c.c. for $NaAlO_2$ in (2a), but found it only at 1.50 c.c. salt, F. Subsequently, there were indefinite breaks (FGHJ), the last one (J) at 2.20 c.c. against 2.1 c.c. expected for $Al(OH)_3$. This situation leaves the possibility for the following reactions open :

$$Al(OH)_3 + NaOH = NaAlO_2 + 2H_2O \quad .. \quad (i)$$
$$Al(OH)_3 + 2NaOH = Na_2HAlO_3 + 2H_2O \quad .. \quad (ii)$$
$$Al(OH)_3 + 3NaOH = Na_3AlO_3 + 3H_2O \quad .. \quad (iii)$$

Precipitation occurs just before G so that the subsequent portion of the graph may be vitiated by adsorption of Al^{3+}. It is not surprising that the extrapolations of FG and KJ produce an intersection at 2.10 c.c., the value expected for pure $Al(OH)_3$. Prasad, Mehta, and Joshi (this *Journal*, 1930, **7**, 973) from their own work pointed out the possibility of formation of Na_2HAlO_3 and Na_3AlO_3, the minimum conductivity corresponding to (*iii*); but this work was not corroborated by that of Britton (*loc. cit.*, p. 141).

This titration was repeated, as stated in (2b). The mixture was heated, as stated in (1b). The first inflection maintained its location, indicating thereby that the salts formed were stable enough not to be affected by heating. The points on the intermediate branch (FGHJ) now fell on a smoother graph and led to the correct value for $Al(OH)_3$ automatically, perhaps indicating decreased adsorption. Similar results were produced when one started with a more dilute solution of alkali (2c).

Back-titration of Excess Alkali.—In a number of titrations we started with salt in the cell to which a known excess of NaOH had been added. This ensured the formation of salts like $NaAlO_2$. The excess alkali was then titrated back with 1*N*-HCl (3a, 3b, 3c). In (3a) the first inflection is at 4.90 equivs. against 5.0 required (NaOH bound) for the reaction (*a*).

Here the alkali : salt ratio was 1:25 at the commencement. When this ratio was reduced to 1:12 in 3b, 3c, the bound alkali dropped to 4.6 equivs. There is therefore no possibility of

FIG. 3

Titration of excess NaOH.

obtaining pure Na_2HAlO_3 by mixing equivalent quantities of the salt and NaOH. These experiments perhaps indicate that Na_2HAlO_3 is quite a stable salt.

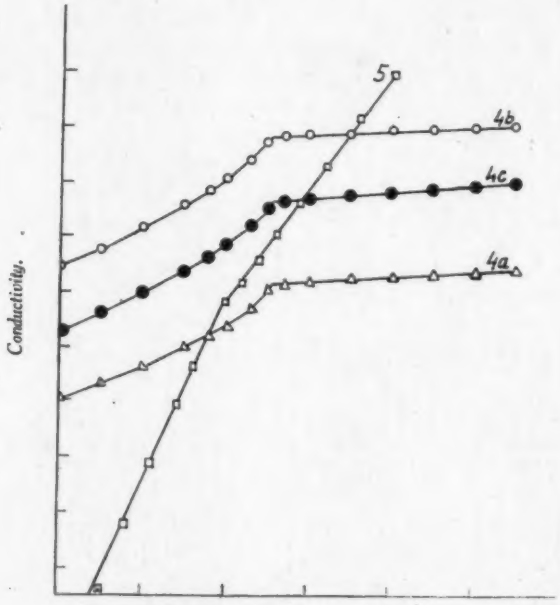
A second inflection occurred at 0, 0.843, 0.843 equiv. NaOH bound respectively in 3a, 3b, 3c. We may conclude that whole of the aluminium taken was converted into $AlCl_3$ in 3a, but this stage was not attained in 3b and 3c. It would be curious if the reaction (*b*) is involved.

$$Al(NO_3)_3 + 5NaOH \rightleftharpoons Na_2HAlO_3 + 3NaNO_3 + 2H_2O \quad .. \ (a)$$

$$AlCl_3 + NaOH \rightleftharpoons Al(OH)Cl_2 + NaCl \quad .. \ (b)$$

One may note that the concentration of Al^{3+} in 3b and 3c was almost double of that in 3a.

FIG. 4



c.c. NH_4OH [(c.c. $NO_3)_3$ *in* 5]

Titration of $Al(NO_3)_3$ *with* NH_4OH (*reverse in* 5)

Titration with Ammonia and the Reverse.—The graphs are shown in Fig. 4. The titrations were satisfactory in neither direction for analytical purposes. The ammonia consumed was always 4% higher than that required for the complete precipitation of $Al(OH)_3$. The precipitation of $Al(OH)_3$ is complete only when the *p*H is about 7 (Vogel, "Quantitative Inorganic Analysis", p. 410, Longmans, Green, 1951), which implies that a slight excess of ammonia must be present. The end point was not affected by the addition of ammonium or potassium chloride in small quantities.

Further work is in progress. One of the authors (B.R.G.) is grateful to the Patna University for a research scholarship.

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GUANYLALKYLUREAS AND THEIR METALLIC COMPLEXES. PART VII. GUANYL*cyclo*HEXYLUREA

By R. L. Dutta and Subrata Lahiry

Guanyl*cyclo*hexylurea and its complexes with copper(II), nickel(II), and palladium(II) have been prepared and their properties studied. The complexes are all of the *bis*-guanylurea type and have the usual colour: copper (rose-red), nickel (yellow to orange), and palladium (pale cream). The copper complex is paramagnetic (μ_{eff} = 1.87 B.M.) whereas the nickel and palladium complexes are diamagnetic. The rose-red copper complex (λ_{max} 530-540 mμ) changes in solution at *p*H 4 to the blue-coloured *mono*guanylurea complex (λ_{max} 660 mμ). It has not been possible, however, to isolate the blue-coloured complex in the pure state.

It has recently been observed in this laboratory that dicyandiamide and an alcohol react in presence of copper salts to form the complex copper salt of the guanylurea with an alkyl substituent, corresponding to that of the alcohol used, at the urea end of the molecule. From the rose-coloured complex the guanylalkylurea was obtained after decomposing with H_2S. Thus several guanylalkylureas, namely, guanyl-methyl-, -ethyl-, -butyl^n-, -butyl^i-, -amyl^i-, hexyl^n-urea sulphates were isolated (Dutta and Rây, this *Journal*, 1959, **36,** 499). A comprehensive study of the copper (II), nickel (II), palladium (II), and cobalt (III) complexes of these ligands has also been made (Dutta *et al.*, *ibid.*, 1959, **36,** 567, 576 ; 1960, **37,** 573 ; Dutta, *ibid.*, 1960, **37,** 499).

It has now been found that dicyandiamide and *cyclo*hexanol react in a similar manner in presence of copper acetate to form the red-violet complex, copper-*bis*-guanyl*cyclo*hexylurea acetate.

From the complex copper sulphate, the reagent guanyl*cyclo*hexylurea sulphate was isolated as colorless crystals, and the nature of the copper (II), nickel (II), and palladium (II) complexes was studied.

Copper (II) gives rise to the usual rose-red anhydro-base in alkaline medium. This is stable towards boiling in aqueous ethanol medium. In addition, several salts of the base, namely, sulphate, chloride, iodide, perchlorate, and acetate, have also been characterised, which are insoluble in water, but as observed with the other substituted guanylalkylureas (*loc. cit.*), most of these complexes (sulphate salt is an exception) are soluble in ethanol. The complexes are paramagnetic ($\mu_{eff} = 1.87$ B.M.). An ethanolic solution of the chloride salt shows an absorption maximum at 530-540 mμ. At a *p*H of about 4, the red-violet colour changes to a blue one (λ_{max} 660 mμ), which is indicative of the existence of a copper-*mono*guanyl*cyclo*hexylurea complex (cf. Dutta, *loc. cit.*). Like the blue complex copper-*mono*-guanylmethyl- and copper-*mono*-guanylethylurea chlorides (Dutta *et al.*, *loc. cit.*, p. 567), it has not been possible to isolate a similar complex in the case of this ligand.

Nickel (II) forms in alkaline medium a yellow anhydro-base. Besides the base, the complex nickel sulphate, chloride, bromide, and iodide have also been isolated. The complexes are diamagnetic, indicating a planar structure, characteristic of penetration complexes of nickel with dsp^2 bonds. The ethanol solution of the chloride salt shows an absorption maximum at 440-450 mμ.

Palladium (II) also forms a pale cream-coloured anhydro-base. The complex sulphate has also been described. Like nickel (II) complexes, palladium (II) complexes are also diamagnetic.

EXPERIMENTAL

*Guanyl*cyclo*hexylurea Sulphate*

Dicyandiamide (5 g.), copper acetate (5 g.), and *cyclo*hexanol (50 c.c.) were heated under reflux on a water bath. The reaction was slow; the characteristic violet colour developed after a few hours. When the reaction mixture became deep violet in colour, it was filtered and the filtrate allowed to stand a day or two in the open with occasional scratching. When fine crystals began to separate, the mixture was left in the frigidaire for a few more days, when the complex copper-guanyl*cyclo*hexylurea acetate crystallised out in quantity. The crystals were filtered, dissolved in hot ethanol (50 c.c.) and treated with an aqueous solution of ammonium sulphate, when the complex copper sulphate was precipitated. The dried complex sulphate was then powdered, suspended in water (10-15 c.c.) and decomposed with H_2S. After removing the CuS, the filtrate was freed of H_2S by air, cooled in ice bath and treated with a large volume of acetone, when colorless crystals of guanyl*cyclo*hexylurea sulphate separated out. These were then filtered and dried over $CaCl_2$. The substance is highly soluble in water. This responds to all the usual tests of guanylurea. (Found: N, 24.45; SO_4, 20.90. $(C_8H_{16}ON_4)_2.H_2SO_4$ requires N, 24.03; SO_4, 20.60%).

*Copper-*bis-*guanyl*cyclo*hexylurea Acetate*

The preceding crude complex copper acetate was purified by recrystallisation from hot ethanol, and then dried in air. {Found: Cu, 10.83; N, 19.60; H_2O (by loss at 110°), 6.50. $[Cu(C_8H_{16}O_4N)_2](CH_3COO)_2, 2H_2O$ requires Cu, 10.84; N, 19.11; H_2O, 6.14%}.

Copper-bis-guanylcyclohexylurea Base

An ethanol solution of the complex copper acetate was treated with an NaOH solution (dil.) when the complex copper base separated as a dull rose precipitate. This was purified by recrystallisation from a large volume of boiling ethanol. It is insoluble in water and sparingly soluble in ethanol or acetone. The compound liberates ammonia from ammonium salts and suffers no loss in weight even at 130°. {Found : Cu, 14.88. $[Cu(C_8H_{15}O_4N)_2]$ requires Cu, 14.78%}.

The *sulphate* was obtained as a rose-red crystalline precipitate, as described earlier. {Found : Cu, 11.52 ; N, 20.80 ; SO_4, 17.30. $[Cu(C_8H_{16}ON_4)_2]SO_4$, H_2O requires Cu, 11.64 ; N, 20.53 ; SO_4, 17.60%}. The substance is paramagnetic. $\chi_g = 2.092 \times 10^{-6}$; $\chi_m = 1141 \times 10^{-6}$; diamagnetic correction $= 273.4 \times 10^{-6}$; $\mu_{eff} = 1.87$ B.M. (temp. 35°).

The following salts of the complex copper base were obtained as rose-red crystals by metathesis of complex copper acetate and the appropriate alkali metal salts in aqueous ethanolic medium and were further purified from ethanol.

Chloride : {Found : Cu, 11.90 ; Cl, 13.31 ; H_2O, 5.20. $[Cu(C_8H_{16}ON_4)_2]Cl_2$, $1.5H_2O$ requires Cu, 11.99 ; Cl, 13.41 ; H_2O, 5.10%}.

Iodide : {Found : Cu, 8.82 ; I, 35.40 ; H_2O, 5.10. $[Cu(C_8H_{16}ON_4)_2]I_2$, $2H_2O$ requires Cu, 8.80 ; I, 35.19 ; H_2O, 4.99%).

Perchlorate : {Found : Cu, 8.82 ; H_2O, 9.90. $[Cu(C_8H_{16}ON_4)_2](ClO_4)_2$, $4H_2O$ requires Cu, 9.04 ; H_2O, 10.25%}.

Nickel-bis-guanylcyclohexylurea Base

It was prepared by digesting on a water bath a solution of nickel sulphate (1 *M*) and freshly prepared guanylcyclohexylurea sulphate solution (1.5 *M* ; obtained as described under the reagent) with dilute alkali solution. The precipitated yellow compound was filtered, washed with water, and dried over KOH. This liberates ammonia from ammonium salts. {Found : Ni, 13.60. $[Ni(C_8H_{15}ON_4)_2]$ requires Ni, 13.82%}.

Chloride.—The complex nickel base was suspended in ethanol and triturated with 2*N*-HCl to a neutral reaction, when a clear, deep orange-red solution was formed. This deposited orange-red crystals on cooling. {Found : Ni, 11.50 ; Cl, 14.12 ; H_2O, 2.00. $[Ni(C_8H_{16}ON_4)_2]Cl_2$, $0.5H_2O$ requires Ni, 11.59 ; Cl, 14.02 ; H_2O, 1.77%}. The compound is diamagnetic. $\chi_g = -0.36 \times 10^{-6}$ (35°). The following salts were obtained as described under copper.

Bromide : {Found : Ni, 10.25. $[Ni(C_8H_{16}ON_4)_2]Br_2$ requires Ni, 10.01%}.

Iodide : {Found : Ni, 8.75 ; I, 37.20. $[Ni(C_8H_{16}ON_4)_2]I_2$ requires Ni, 8.62 ; I, 37.30%}.

Sulphate : {Found : Ni, 10.80 ; SO_4, 17.85 ; H_2O, 2.90. $[Ni(C_8H_{16}ON_4)_2]SO_4$, H_2O requires Ni, 10.85 ; SO_4, 17.75 ; H_2O, 2.90%).

Palladium-bis-guanylcyclohexylurea Base

It was obtained as a pale cream precipitate by the action of alkali on a mixture of sodium chloropalladite ($PdCl_2$, 1 *M*) and the reagent (1.5 *M*). {Found : Pd, 22.60 ; N, 23.54. $[Pd(C_8H_{15}ON_4)_2]$ requires Pd, 22.48 ; N, 23.59%}.

Sulphate.—The complex palladium base was suspended in ethanol, neutralised with HCl (dil.), filtered, and then treated with aqueous ammonium sulphate. The precipitated complex sulphate was filtered, washed with water and ethanol, and dried in air. {Found : Pd,18.30 ; SO_4, 16.20 ; H_2O, 3.00. $[Pd(C_8H_{16}ON_4)_2]SO_4, H_2O$ requires Pd, 18.12 ; SO_4, 16.30 ; H_2O, 3.05%}. The substance is diamagnetic. $\chi_g = -0.33 \times 10^{-6}$ (31°).

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STUDIES ON THE ADSORPTION OF HUMIC ACID ON H-CLAYS AND THE ROLE OF METAL CATIONS IN HUMUS ADSORPTION

By B. C. Sen

Adsorption of humus by H-clay in different proportions of their mixtures and the role of metal cations in humus adsorption have been studied thoroughly. The results establish two types of linkages between clay and humus—one is a weak bonding where humic acid can be easily extracted by alkali treatment and the other, a strong bonding corresponding to alkali non-extractable portion, where clay, humic acid, and the added cation are involved.

In a previous communication (*Ind. J. Appl. Chem.*, 1960, **23,** 145) it has been shown from base-exchange measurements that humic acid and clay minerals do interact leading to a decrease of b.e.c., but the exact nature of this interaction is not clear from this study. In the colloidal state both humic acid and clay are negatively charged. Consequently, mutual coagulation is out of the question. Under the conditions of the experiments an exchange of humate ions for lattice OH does not appear very likely. There is another possibility of a certain kind of co-ordination of the anionic colloidal species with a common cation. This possibility has been studied by determining the adsorption of humic acid by clays in presence of different cations.

Sideri (*Soil Sci.*, 1936, **42,** 461 ; 1938, **46,** 129) has observed that the amount of humus, irreversibly adsorbed by a clay, depends on the character of the clay, whereby mixed clay-humus micelles are formed in which majority of the clay particles possess a fairly definite orientation. According to Jung (*Bodenk. Pfl. Frnahr*, 1943, **32,** 325) the adsorption of humus materials by clays could be better expressed by a hyperbolic function than by the adsorption isotherm. The observations of Sideri (*loc. cit.*), Jung (*loc. cit.*), Myers (*Forsch. Dienst. Sonderh*, 1941, **17,** 38), Khan (*Pedology*, U.S.S.R., 1950, 673 ; *Doklady Akad. Nauk*, U.S.S.R., 1951, **81,** 461) and others have shown that in the clay-humus combination there should be some loose chemical linkage apart from the general van der Waals type of adsorption. A few workers (Hideaki Saeki, *Jap. Assoc. Advanc. Sci.*, 1942, **16,** 410 ; Khan, *loc. cit.*) also studied the importance of metal ions in this bonding. This aspect of the problem calls for a systematic study, which has been attempted here.

Experimental

Clay and humic acid sols were prepared as described previously (Sen, *loc. cit.*). The clay fractions ($< 1\mu$) from 5 different soil samples were collected in the usual way. The *p*H values of about 2.5% clay sol varied between 3.5 and 4.2. Humic acid was extracted from Padegaon B soil. The *p*H value of approximately 0.6% humic acid sol was found to be 3.5. The b.e.c. values of the pure H-clay and humic acid sol were determined by *p*H titration from the amount of baryta corresponding to the inflection point and reported in the earlier communication (Sen, *loc. cit.*, Table I).

The adsorption was studied in the following way. The mixtures of clay and humic acid sols in the desired proportions were kept for about a week with occasional shaking. Preliminary studies, allowing time of reaction longer than about a week, did not show any further appreciable change in the titration curves and other properties of the mixtures. Usually therefore one week's time was allowed for the interaction to proceed. Then an aliquot of each of the mixtures was taken out, and the loosely bound or adsorbed portion of humic acid was extracted by washing repeatedly with $N/2$- Na_2CO_3 solution and centrifuged until the Na_2CO_3 extract was no longer coloured with humic acid. In the collected washings the amount of humic acid was analysed by the

method of Walkley and Black (*Soil Sci.*, 1934, **37**, 29), in which the organic matter was decomposed with chromic acid, and the residual chromic acid was titrated back with a standard Mohr salt solution using diphenylamine as indicator. Similar experiments were performed in presence of Ca^{2+}, Mg^{2+}, Al^{3+}, and Fe^{3+} ions. The amount of the respective ions added corresponds to the total exchange capacity of the clay-humic acid mixture. The cations were added in the form of chloride or sulphate, and it is likely that depending on the condition of ionic equilibrium, all the ions will not take part, if at all, in the interaction. Added in the form of oxides or hydroxides, e.g., those of Ca and Mg, the reaction is likely to be complete, as a neutralisation reaction is. In one set of experiments therefore, viz., in case of PBM clay and AGM clay, the Ca^{2+} was added in the form of hydroxide (added in amount equivalent to the b.e.c. of the mixture), and clay-humus interaction was studied in its presence just like in other cases. Then a known aliquot of each was leached several times with 200-250 c.c. of NaCl(*N*) solution as in the determination of exchangeable Ca^{2+}. In the leachate the amount of calcium was determined by precipitation as oxalate, followed by $KMnO_4$ titration. The results of the above experiments are reported in Tables I and II and in Figs. 1-5.

TABLE I

Estimation of alkali-extractable humic acid from clay-humic acid mixtures.

Ions present.	Humic acid: clay.	% Humic acid combined* with different clays.				
		PBM.	AGM.	CL	KL	RK.
H^+	1:10	30	36	20	18	12
	1:20	36	42	25	20	16
	1:40	40	50	29	25	20
	1:60	48	55	35	32	23
Ca^{2+}	1:10	38	45	28	25	18
	1:20	48	55	35	31	24
	1:40	60	68	40	37	29
	1:60	65	73	46	42	32
Mg^{2+}	1:10	44	55	35	30	22
	1:20	60	65	42	37	26.5
	1:40	70	75	47	43	33
	1:60	75	82	55	48	37
Al^{3+}	1:10	42	53	35	30	23
	1:20	56	63	40	36	27
	1:40	69	73	46	44	33
	1:60	72	82	54	48	36
Fe^{3+}	1:10	45	55	37.5	32	25
	1:20	62	66	44	38	29
	1:40	70	78	48	46	34.5
	1:60	74	83	58	50	38

N.B. For symbols vide Sen, *loc. cit.*

* Not extractable by Na_2CO_3 leaching.

TABLE II

Estimation of calcium extracted with N-NaCl solution from the PBM clay-and AGM clay-crude humic acid mixtures prepared in presence of CaO.

Humic acid: clay.	CaO added.	CaO in NaCl leachate.	
	PBM clay + humic acid.		
1:10	0.0436 g.	0.0166 g.	38%
1:20	0.0343	0.0133	39
1:40	0.0414	0.0156	38
1:60	0.0340	0.0103	30
	AGM clay + humic acid.		
1:10	0.0322	0.0122	38
1:20	0.0277	0.0111	40
1:40	0.0510	0.0214	40
1:60	0.0249	0.0095	38

DISCUSSION

The results obtained definitely show that a portion of the adsorbed humic acid is not extractable by alkali treatment. This strong bonding between clay and humus is probably of a chemical

FIG. 1

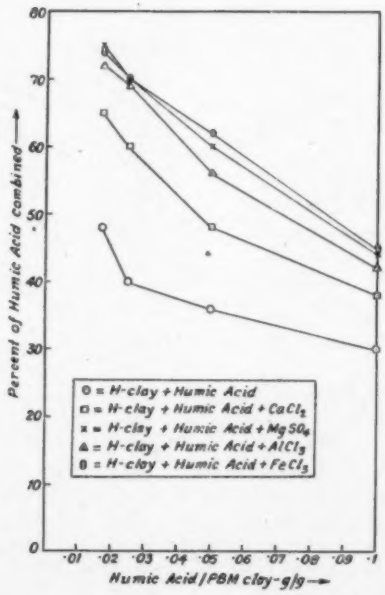
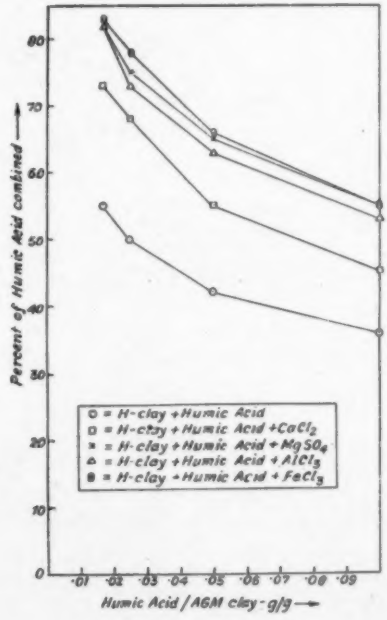

Percent of Humic Acid combined
Humic Acid / PBM clay - g/g
○ = H-clay + Humic Acid
□ = H-clay + Humic Acid + CaCl2
× = H-clay + Humic Acid + MgSO4
△ = H-clay + Humic Acid + AlCl3
⊖ = H-clay + Humic Acid + FeCl3

FIG. 2


Percent of Humic Acid combined
Humic Acid / AGM clay - g/g
○ = H-clay + Humic Acid
□ = H-clay + Humic Acid + CaCl2
× = H-clay + Humic Acid + MgSO4
△ = H-clay + Humic Acid + AlCl3
⊖ = H-clay + Humic Acid + FeCl3

nature. As the proportion of humic acid decreases in the mixtures, not only is the interaction more extensive but also the intensity of interaction increases appreciably. This is shown by the gradually increasing amounts of combined humic acid with smaller proportions of it.

The interaction is also dependent on the nature of the cation present in the mixture. Mg^{2+}, Al^{3+}, and Fe^{3+} ions have nearly the same effect, viz., considerable increase in the amount of combined humic acid. H^{+} ion is least effective whereas Ca^{2+} ion is intermediate. The nature of the clay mineral determines to a certain extent the intensity of interaction. In illite (CI sample) the proportion of combined humic acid is much smaller than in montmorillonite (PBM and AGM clay samples), but the order of effectiveness of the cations is the same. In kaolinite (RK clay) the intensity of interaction is the least, but here also the order of effectiveness of the cations remains the same. Between the two samples of montmorillonites, the strength of binding of humic acid is somewhat greater in AGM clay than in PBM clay. It may be noted that the crude humic acid used in these two cases was extracted from the original PBM soil (Sen, *loc. cit.*, Table I). Apparently, the higher b.e.c. of AGM clay is responsible for the stronger combination.

FIG. 3

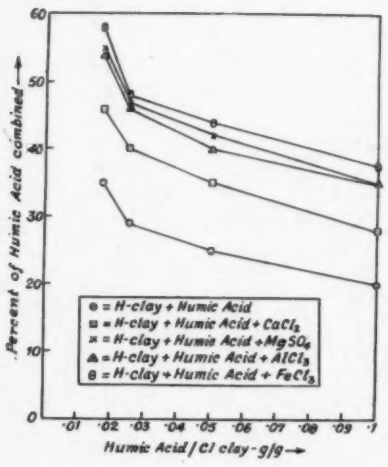
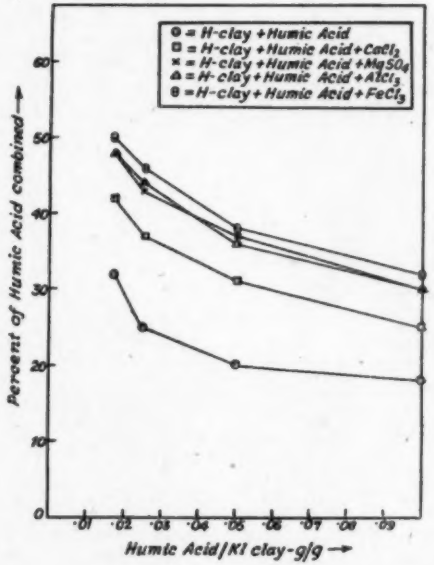
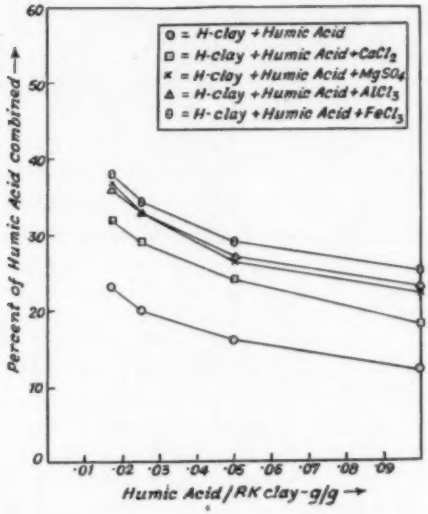

Percent of Humic Acid combined →
Humic Acid / CI clay - g/g →
⊙ = H-clay + Humic Acid
□ = H-clay + Humic Acid + CaCl2
× = H-clay + Humic Acid + MgSO4
△ = H-clay + Humic Acid + AlCl3
θ = H-clay + Humic Acid + FeCl3

FIG. 4


Percent of Humic Acid combined →
Humic Acid / KI clay - g/g →
⊙ = H-clay + Humic Acid
□ = H-clay + Humic Acid + CaCl2
× = H-clay + Humic Acid + MgSO4
△ = H-clay + Humic Acid + AlCl3
θ = H-clay + Humic Acid + FeCl3

From the estimation of calcium in NaCl leachate, obtained from different clay-humus mixtures, it is seen that in every case an appreciable part of calcium added has been retained by the clay-humic acid complex. Had this calcium been present in the exchangeable position, it could have been completely leached out by the NaCl solution. Hence this suggests that part of the calcium ions is present in a non-exchangeable form in the complex, formed between humic acid and clay minerals.

FIG. 5


○ = H-clay + Humic Acid
□ = H-clay + Humic Acid + $CaCl_2$
× = H-clay + Humic Acid + $MgSO_4$
△ = H-clay + Humic Acid + $AlCl_3$
θ = H-clay + Humic Acid + $FeCl_3$
Percent of Humic Acid combined →
60
50
40
30
20
10
0
·01 ·02 ·03 ·04 ·05 ·06 ·07 ·08 ·09
Humic Acid / RK clay - g/g →

It may be concluded from the above observations that there must be two types of linkages between clay and humus. One is a weak bonding where perhaps the humic acid is present as a coating on the outermost surface of the clay micelle, and, as a result, it is easily extractable by alkali treatment. The other is a strong bonding corresponding to the alkali non-extractable portion where clay, humic acid, and the added cations are involved. It is likely that this clay-humus complex is formed in such a manner that the OH and COOH groups of humic acid co-ordinate with the metal ions occupying the exchangeable positions in the clay-mineral lattice.

Thanks are due to Prof. S. K. Mukherjee, D.Sc., Professor of Macromolecules, Indian Association for the Cultivation of Science, for his guidance and valuable suggestions and to Prof. P. C. Rakshit, Ph.D., Head of the Dept. of Chemistry, Presidency College, for his continued interest and for providing laboratory facilities.

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SHORT NOTES

PREPARATION OF URANIUM(IV) OXYACETATE

BY N. C. NAIK, BALARAM SAHOO AND D. PATNAIK

Preparation of two hydrated uranium(IV) oxyacetate possessing the formula $UO(CH_3COO)_2 \cdot H_2O$ (Tripathy *et al.*, this *Journal*, 1959, **36**, 739) and $UO(CH_3COO)_2 \cdot 2.5H_2O$ (Sahoo and Patnaik, *Curr. Sci.*, 1960, **29**, 16) was reported earlier. As these compounds were obtained in fine state of division, considerable difficulty was experienced in the filtration process; further, as much of the uranium remained in solution, the product was never quantitative. The method described below obviates the difficulty of filtration and makes the yield almost quantitative.

As before, the solution of uranyl acetate was subjected to photochemical reduction on exposure to sunlight (*loc. cit.*). Distillation of the reduced solution was next carried out under reduced pressure at about 80°, when uranium(IV) oxyacetate was precipitated in a fine form. The distillation was continued till the solution left was just enough to keep the precipitate moist. The compound was dried in vacuum at room temperature. Analysis was carried out as described previously (*loc. cit.*). The data recorded in Tables I and II show that the compound obtained possesses the formula $UO(CH_3COO)_2 \cdot 1.5H_2O$. The molecular weight from the three prepared samples was calculated from the U_3O_8 obtained and the values found were 399.9, 400.4, and 399.6 in place of the theoretical value 399.

It may be noted that the different methods of preparation have given rise to compounds associated with different number of water molecules although the method of drying remains the same.

TABLE I

$UO(CH_3COO)_2 \cdot 1.5H_2O$.

U(IV) content by $KMnO_4$.			Acetate by hydrolysis.		
Taken.	Found.	Calc.	Taken.	Found.	Calc.
289.0 mg.	171.5 mg.	172.4 mg.	257.6 mg.	76.17 mg.	76.47 mg.
369.8	220.3	220.6	442.4	131.0	130.8
186.8	111.6	111.4	640.0	190.2	189.2

TABLE II

Estimation of carbon and hydrogen.

Compound taken.	Weight of water.		Weight of CO_2.	
	Found.	Calc.	Found.	Calc.
136.8 mg.	27.6 mg.	27.8 mg.	61.0 mg.	61.4 mg.
91.0	18.2	18.47	40.0	40.14

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CHALKONES. STUDIES IN THE CLAISEN-SCHMIDT CONDENSATION

BY DURGA NATH DHAR*

The effect of three substituent groups, viz., hydroxyl, methoxyl and methyl, substituted in the aldehyde component and hydroxyl in the ketone component, on the Claisen-Schmidt condensation has been studied.

The chalkones were prepared according to the procedure of Schraufstatter and Deutsch (*Chem. Ber.*, 1948, **81,** 489). The procedure consists in the addition of about 50% aqueous KOH to benzaldehyde and acetophenone derivative in ethanol and heating at 60° for 2 hours on a water bath. The chalkones were isolated in the usual way. The %yield of various chalkones, obtained under identical conditions, are recorded in Table I.

TABLE I

Ketone.	B.	Hydroxy-B.			Methoxy-B			Dimethoxy-B		Hydroxy-methoxy-B		Methy -		
		o-	*m-*	*p-*	*o-*	*m-*	*p-*	2:3-	3:4-	4:3-	2:3-	*o-*	*m-*	*p-*
Resaceto-phenone	41.4	4.5	28.6	..	81.9	33.9	46.9	69.0 71.8	33.2	..	10.9	60.5	50.9	64.1
o-Hydroxy-acetophenone	64.6	34.6	69.0	23.6	85.6	60.9	69.5	61.2	64.4	19.9	48.6	48.5 49.5	52.6	66.7
Acetophenone	‡	63.5	47.7*	53.3	86.1	83.7	88.6	85.6	76.2	48.8	73.0	‡	‡	‡

B represents benzaldehyde.
‡ Abnormal condensation occurs.
* Side reaction takes place.
N.B.—Condensation failed to occur with resorcylaldehyde.

As no definite generalisation can be drawn to cover all the experimental data recorded in Table I, only the significant conclusions arrived at are given :

In general, the introduction of OH-group, in either of the reacting molecules, retards or sometimes completely inhibits the Claisen-Schmidt condensation. Examples are the condensation of resacetophenone or *o*-hydroxyacetophenone with salicylaldehyde and resorcylaldehyde.

Nevertheless, the presence of OH-group, particularly in the ketone component, prevents the formation of undesirable products. Thus resacetophenone and *o*-hydroxyacetophenone condense normally with benzaldehyde and isomeric tolylaldehydes to yield the respective chalkones; on the other hand, the interaction of acetophenone with the above mentioned aldehydes does not lead to the formation of chalkones under the experimental conditions employed. Formation of chal-

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kones in the above condensation can, however, be secured by using a milder concentration of alkali and carrying out the reaction at a lower temperature (Kohler and Chadwell, "Org. Syntheses", Vol. II, 1922, p. 1; Weygand and Schacher, *Ber.*, 1935, **58B,** 227).

Replacement of the OH-group by either methyl or methoxy (in the aldehyde component) results in increase in yield of the chalkone.

The author thanks Dr. J. B. Lal for interest in this work and the Government of India, Ministry of Scientific Research and Cultural Affairs, for the award of a senior research scholarship.

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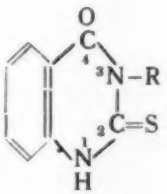
SYNTHESIS OF SOME 2-THIO-3-(SUBSTITUTED) BENZYL-QUINAZOLINE-2 :4(1H, 3H)-DIONES

By J. P. Trivedi

Thioquinazolones are physiologically active compounds. Gujral and Saxena (*Chem. Abst.*, 1956, **50,** 6662) tested some 2-alkyl-3-phenyl-4(3H)-quinazolones and found them active as ataractic agents. Buzas and Hoffman (*Bull. Soc. Chim.*, 1959, 1889) also synthesised 2-alkyl-3-substituted-4(3H)-quinazolones as potential hypnotics and analgesics. Very recently McCarty *et al.* (*J. Amer. Chem. Soc.*, 1960, **82,** 964) prepared a series of 2-alkylthio-3-phenyl (or allyl)-4-(3H)-quinazolones. Benzyl *iso*thiocyanates were first prepared and reported by the present author (this *Journal*, 1956, **33,** 423), some of which have been patented as bacteriostatic agents (McKay and Garmaise, Canad. Patent, No. 579233; *Chem. Abst.*, 1960, **54,** 412; *J. Amer. Chem. Soc.*, 1959, **81,** 4328). Since benzyl *iso*thiocyanate moiety will also be present in 2-thio-3-(substituted) benzylquinazoline-2: 4-(1H, 3H)-diones, it is of interest to synthesise a series of these compounds as potential ataractic agents for studying their activity. Table I describes the compounds prepared.

TABLE I



No.	R.	Crystalline nature.	M.P.	% Sulphur Found.	Calc.
1.	$C_6H_5CH_2$ *	Colorless needles	246°	11.8	11.9
2.	o-$ClC_6H_4CH_2$	,,	262°	10.6	10.6
3.	p-$ClC_6H_4CH_2$		226°	10.5	10.6
4.	p-$BrC_6H_4CH_2$	,,	220°	9.1	9.2
5.	p-$IC_6H_4CH_2$	,,	268-70°	7.9	8.1
6.	m-$CH_3C_6H_4CH_2$	Colorless granules	216°	11.1	11.3
7.	$(CH_3)_2$ $C_6H_3CH_2$ (2:5)	,, needles**	259-60°	10.7	10.8
8.	$(CH_3)_2$ $C_6H_3CH_2$ (2:4)	Yellowish granules	235°	10.6	10.8

* Repeated crystallization from benzene and ethanol.

** Required six hours' refluxing.

General Method of Preparation.—Substituted benzyl *iso*thiocyanates (0.1*M*), dissolved in absolute ethanol, were slowly added to an ethanolic solution of anthranilic acid (0.1*M*.) in a r.b. flask, and the reaction mixture refluxed on a water bath until the smell of *iso*thiocyanate disappeared (usually 2-3 hours). The reaction product was transferred to a beaker and the alcohol allowed to evaporate whereupon crystalline thioquinazolones separated out. These were recrystallised from ethanol until analytically pure samples were obtained. The compounds prepared are listed in the table. All melting points are uncorrected.

Synthesis of 2-alkyl and aryl thio-3-substituted benzylthioquinazolones, their hydrolysis to obtain the corresponding quinazoline diones and synthesis of 1: 3-thiazines from these compounds are in progress and will be communicated in future.

The author thanks Dr. N. M. Shah for interest in this work and the Principal for facilities.

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A NEW COMPLEX COMPOUND OF RHENIUM

By R. D. Daftary and B. C. Haldar

A new complex compound of rhenium has been prepared by the interaction of diphenylcarbazide and potassium perrhenate. When acetone solution of diphenylcarbazide is added slowly to ice-cold potassium perrhenate solution in 8*N*-HCl, deep violet solids are formed. These are separated after an hour by centrifugation, dissolved in minimum quantity of acetone, and reprecipitated by dropwise addition of 10*N*-HCl. The solids are removed, washed twice with ice-cold water, and then taken up in chloroform. Any residue remaining is rejected.

The violet coloured compound is obtained by evaporation of the chloroform solution. On drying at 110° it loses weight and changes into a substance, insoluble in chloroform. So it is dried in a vacuum disiccator. It is insoluble in water but soluble in organic solvents, such as, acetone, acetophenone, etc.

Transport experiment with acetone solution of the complex, containing free hydrochloric acid, indicates that it is a non-electrolyte. The results of chemical analysis of the compound suggest its formula as $[Re(OH)_2Cl_2DPO]_x$, where DPO represents a molecule of diphenylcarbazone less one hydrogen atom, and x is an integer. {Found : C,28.86; H, 2.24; O (by diff), 10.62; N, 9.98; Cl, 13.2; Re, 35.1. $[Re(OH)_2Cl_2\ DPO]_x$ requires C, 29.43; H, 2.47; O, 9.05; N, 10.56; Cl, 13.37; Re, 35.12%}. The value of x in the empirical formula of the complex has been determined from the depression of the freezing point of acetophenone and is found to be 0.88, suggesting the simple formula $[Re(OH)_2Cl_2DPO]$ for the complex. Magnetic susceptibility measurements show that the complex is diamagnetic.

The absorption spectra of the complex in acetone and chloroform solutions show maxima at around 540 mμ in the visible region; the molar extinction coefficients of the complex in acetone and chloroform solutions, measured at 540 mμ, are 6853 and 6619 $mol^{-1}cm^{-1}$ respectively. Absorption measurements have been taken with Unicam S.P. 500 spectrophotometer using 1 cm cells. Although the compound is insoluble in water, the violet colour of the acetone solution disappears by the addition of water. Fruther work is in progress.

The authors express their sincere thanks to Prof. P. B. Sarkar, Head of the Chemistry Department, Calcutta University, for giving laboratory facilities for magnetic measurements and to Principal, Y. G. Naik for allowing them to use the spectrophotometer of the Physics Department, Gujarat College, Ahmedabad. Grateful acknowledgements are due to the Ministry of Scientific Research and Cultural Affairs, Government of India, for the award of a senior research scholarship to one of them (R. D. Daftary).

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A NEW METHOD FOR THE PREPARATION OF SELENIUM DIOXYDIFLUORIDE, SeO_2F_2

BY GRIHAPATI MITRA

Selenium, unlike sulphur, yields only a few compounds in the highest state of oxidation. SeF_6, unstable SeO_3, and selenates, e.g., salts of SeO_4^{2-}, are the only few known compounds of hexavalent selenium. Recently fluoroselenates, e.g. salts of SeO_3F^{1-}, pentafluoroselenium hypofluorite, F_5SeOF, and *bis*-pentafluoroselenium peroxide, $F_5SeO.OSeF_5$, have been described (Mitra *et al.*, *Science & Culture*, 1955, **20,** 351 ; *J. Amer. Chem. Soc.*, 1959, **81,** 2646).

Sulphuryl fluoride, SO_2F_2, a stable compound of hexavalent sulphur, is known for a long time. The corresponding selenium compound, SeO_2F_2, has recently been prepared by digesting one mole of $BaSeO_4$ with 14 moles of HSO_3F at 50° (Englebrecht and Stoll, Z. *anorg. allgem. Chem.*, 1957, **292,** 20). Another method for the preparation of the same compound is by boiling SeO_3 with excess AsF_3 under reflux for many hours (Jerschkewitz, *Angew. Chem.*, 1957, **69,** 562).

Selenium dioxydifluoride, SeO_2F_2, was also prepared in this laboratory by fluorinating SeO_2 in AgF_2—AgF catalytic chamber. The present note describes the method of preparation in details.

Procedure.—Powdered selenium dioxide was taken in a copper vessel (about 500 c.c.) fitted with an inlet and an outlet tube. The vessel was heated to about 200°. The vapour pressure of SeO_2 at this temperature is about 54 mm. Dry nitrogen gas was passed into the vessel and the outlet tube, which was of very short length, was directly connected to a big nickel tube of about a meter long and 5″ in diameter.

This nickel tube, acting as a catalytic chamber, was filled with copper turnings, very finely plated with silver.*

The catalytic chamber was heated to about 100° and a large excess of fluorine, carried by nitrogen gas, was introduced inside through another inlet tube. After leaving the chamber the gas was passed through a glass trap, cooled externally by liquid oxygen. Fluorine was used in such excess that unchanged fluorine emerged from the condenser trap.

The product was found to be a mixture of (*a*) SeF_6 (excess), (*b*) SiF_4 (appreciable), (*c*) SeO_2F_2 (moderate), (*d*) $SeOF_6$ (?), and (*e*) a residue boiling above 0°, possibly containing various oxyfluorides such as $SeOF_2$, $Se_2O_2F_{10}$, etc.

Separation of SeO_2F_2.—The mixture taken in a pyrex tube was kept immersed in acetone and dry ice. SiF_4 and partly SeF_6 were thus removed. The mixture was then distilled under a little pressure with a fractionating column of about 4′ height and packed with nickel balls. After removal of $SeOF_6$ and SeF_6 a compound was found to boil nearly at—10° at normal pressure.

The molecular weight was determined by vapour density method. The average experimental value found was 149.2 (the theoretical value is 148.9). The compound during second distillation was found to boil at about -9°.

This work was done in late 1955 and early 1956, at the Fluorine Chemistry Laboratory, University of Washington, Seattle, under the guidance of Prof. G. H. Cady, and supported by the office of Naval Research, U.S.A.

*For the detailed description of the Catalytic Chamber the original papers of Cady *et. el.* should be consulted.

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MONOFLUOARSENATES AND THEIR ANALOGY WITH SULPHATES. BASIC MONOFLUOARSENATES OF BIVALENT METALS (Cu & Ni)

By N. K. Dutt and Ashim Gupta

It has been shown previously by the authors ((Z. *anorg. allgem. Chem.*, 1955, **285,** 92) that the monofluoarsenate ion is analogous to sulphate ion, being isoelectronic isosters, in the salts of monovalent and bivalent metals. From the above observations, the study of the basic salts of monofluoarsenates was deemed necessary to extend the above analogies. Considering broadly, the basic salts are the results of the action of a neutral salt with the oxide or hydroxide of the corresponding metal. Numerous investigators worked on the problem of basic salts, especially of those of copper. Various studies have been made on the basic sulphates of copper. Binder (*Compt. rend.*, 1934, **198,** 653) from the phase rule has obtained the basic sulphate, $CuSO_4 . 3\,CuO$. It has been supported by X-ray examination. Conductometric and potentiometric methods were used by Chretien and Heubel (*ibid.*, 1944, **219,** 363) and Marie-Lousier-Brouty (*ibid.*, 1944, **219,** 931) respectively to study the basic sulphate formation of copper. Both methods indicate the formation of the basic salt, $CuSO_4 . 3CuO$, but they fail to give any indication of the formation of the basic salt $CuSO_4 . CuO$. Mitra (this *Journal*, 1955, **32,** 43) obtained one basic fluoberyllate of copper having the composition $CuBeF_4 . 4CuO$ and similarly for nickel. Fluoberyllate ion is quite analogous to sulphate ion and also to monofluoarsenate ion.

Attempts have been made in this laboratory to prepare the basic monofluoarsenates of copper and nickel; a few of these have been described in the present paper.

Ammonium Acetate Method.—In this method, about *M*/5 solutions of the salt and ammonium acetate were mixed in 1 : 4 proportions and left aside for several days. An insoluble precipitate appeared, which was filtered, washed with water and ethanol, and dried in the folds of filter paper.

Preparations were also tried by the method of Guy and Gire (*Compt. rend.*, 1935, **200,** 1213) and of Lamure (*ibid.*, 1945, **220,** 601) using magnesium powder, the function of which is to neutralise the free acid liberated and to maintain a higher *p*H throughout. The following salts have been prepared.

(*a*). $CuAsO_3F . 4\,Cu(OH)_2 . 8\,H_2O$.—It is insoluble in water, light blue in colour and when heated to higher temperatures, it losses its water of hydration, followed by decomposition with evolution of vapour of arsenic. (Found : Cu, 42.82 ; As, 10.18 ; F, 2.64. Calc. Cu, 42.98 ; As, 10.14 ; F, 2.56%).

(*b*). $NiAsO_3F$, $4\,Ni(OH)_2$, $5\,H_2O$.—Same as above. (Found : Ni, 44.36; As, 11.40 ; F, 2.93. Calc. Ni, 44.30 ; As, 11.34 ; F, 2.87%).

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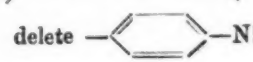
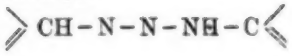
355	Table I, structure (I)		
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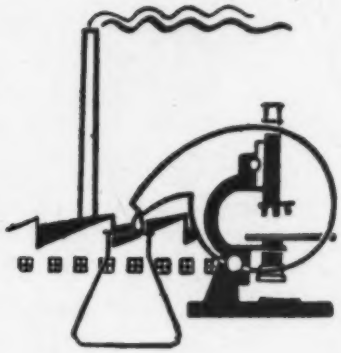

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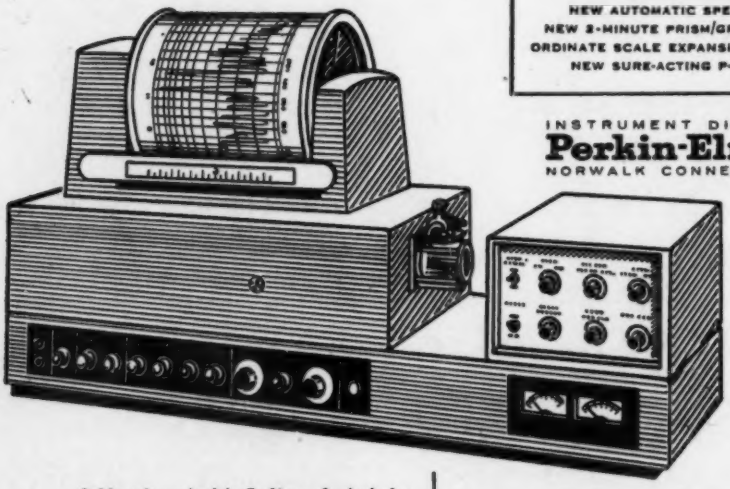

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